SOURCE APPORTIONMENT AND FORECASTING OF AEROSOL IN A STEEL CITY- CASE STUDY OF ROURKELA

A THESIS SUBMITTED BY

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CERTIFICATE

This is to certify that the thesis entitled "**Assessment and modeling of particulate air pollution in Rourkela steel city**" submitted by **Mr. Naga Chaitanya Kavuri**, in partial fulfillment of the requirements for the award of Doctor of Philosophy in Civil Engineering, at National Institute of Technology, Rourkela is an authentic work carried out by him under our supervision and guidance.

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I dedicate this thesis to my dearest friend who is no more with us…

Deepu … may your soul rest in peace

Naga Chaitanya Kavuri

ABSTRACT

Urban air pollution is one of the biggest problems ascending due to rapid urbanization and industrialization. The improvement of air quality in an urban area in general, constitutes of three phases, monitoring, modeling and control measures. The present research work addresses the requirements of the urban air quality management programme (UAQMP) in Rourkela steel city. A typical UAQMP contains three aspects: monitoring of air pollution, modeling of air pollution and taking control measures. The present study aims to conduct the modeling of particulate air pollution for a steel city. Modeling of particulate matter (PM) pollution is nothing but the application of different mathematical models in source apportionment and forecasting of PM. PM (PM_{10} and TSP) was collected twice a week for two years (2011-2012) during working hours in Rourkela. The seasonal variations study of PM showed that the aerosol concentration was high during summer and low during monsoon. A detailed chemical characterization of both PM_{10} and TSP was carried out to find out the concentrations of different metal ions, anions and carbon content. The Spearman rank correlation analysis between different chemical species of PM depicted the presence of both crustal and anthropogenic origins in particulate matter. The enrichment factor analysis highlighted the presence of anthropogenic sources. Three major receptor models were used for the source apportionment of PM, namely chemical mass balance model (CMB), principal component analysis (PCA) and positive matrix factorization (PMF). In selecting source profiles for CMB, an effort has been put to select the profiles which represent the local conditions. Two of the profiles, namely soil dust and road dust, were developed in the present study for better accuracy. All three receptor models have shown that industrial (40-45%) and combustion sources (30-35%) were major contributors to particulate pollution in Rourkela. Artificial neural networks (ANN) were used for the prediction of particulate pollution using

meteorological parameters as inputs. The emphasis is to compare the performances of MLP and RBF algorithms in forecasting and provide a rigorous inter-comparison as a first step toward operational PM forecasting models. The training, testing and validation errors of MLP networks are significantly lower than that of RBF networks. The results indicate that both MLP and RBF have shown good prediction capabilities while MLP networks were better than that of RBF networks. There is no profound bias that can be seen in the models which may also suggest that there are very few or zero external factors that may influence the dispersion and distribution of particulate matter in the study area.

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CHAPTER 1- INTRODUCTION

1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Pollution in the air we breathe is one among the most challenging issues of today's environment. Many types of air pollution are contributing to problems like human health concerns and climate change. Rapid increase in urban population has resulted in increasing pollution load in cities. Between 1951 and 2011, the urban population has quadrupled, from 62.4 million to 377.1 million, and its proportion has grown from 17.3% to 31.16% (Census-India 2011). In 1991, there were 18 cities with a population of over 1 million and in 2012 this number is estimated to increase up to 46 cities. It further resulted in an increase in consumption patterns and higher demand for transport, energy and other infrastructure, thereby putting a load on air pollution problem (Sood 2012).

Central pollution control board of India (CPCB 2010) has reported that growing cities, increasing traffic, trajectory growth, rapid economic development and industrialization with higher levels of energy consumption has resulted in an increase in pollution load in an urban environment. One of the major environmental risks to health is found to be air pollution. In 2012, an estimation of approximately 3.7 million premature deaths worldwide per year have been attributed to air pollution (WHO 2014). Besides health effect, air pollution also contributes to tremendous economic losses, especially in the sense of financial resources that are required for giving medical assistance to the affected people.

Due to rapid urbanization and industrialization ambient air acquires three forms of air pollutants. These are ozone or smog, particulate pollution and gaseous pollutants. Most

ozone is formed by a chemical reaction between sunlight and vapors emitted by burning processes. Any process that increases the temperature of air (N_2+O_2) results in high levels of NO_x which then form O_3. Ozone pollution is generally highest during sunniest months of the year. This pollutant can cause short term health issues immediately following exposure, such as irritation to skin and the respiratory system. With long term exposure it can also lead to more serious health problems, such as impaired lung function, inflammation of the lung lining, and higher rates of pulmonary diseases (Lippmann 1989). Particulate air pollution is most dangerous to human health and it is very widespread throughout the environment. This type of air pollution consists of solid and liquid particles made up of ash, metals, soot, diesel exhaust, and chemicals. PM pollution is produced by coke ovens in steel plants, power plants and other industries and by use of diesel fuel in passenger vehicles, cargo vehicles and heavy equipment(Gartrell and Friedlander 1975). Capable of triggering strokes, heart attacks, and irregular heart rates, particle pollution can be dangerous even in low concentrations. Lung cancer and premature birth have also been linked to exposure to particle pollution and it is known to irritate respiratory conditions, including asthma, coughing, wheezing, and even shorter life spans (Pope 3rd et al. 1995). Other common air pollutants that can pose health risks to humans are gases like carbon monoxide, nitrogen oxides and sulfur dioxide.

Thus, it is important to frame the policy by the government that can allow the city to develop at a comfortable pace without damaging the environment. With rapid modernization, the contribution of various sources to ambient air pollution levels have to be examined so that the most effective sources of pollution can be determined and necessary action can be taken. To achieve this, a detailed chemical characterization of the particulate matter such as heavy metals, non-metals, ions, organic carbon and molecular markers needs to be studied. Along with source contributions the comfort of having forecasting analysis of air pollution will have a great influence on decision making process of air pollution control.

1.2 PARTICULATE MATTER POLLUTION

Particulate matter or PM, is a combination of fine solids and aerosols that are suspended in the air we breathe. Unlike gases, which have defined chemical structure and therefore show certain physical properties, particles in the urban atmosphere vary in size, shape, and chemical composition. Their concentrations in ambient air may therefore be quantified by different measures like number, surface or mass concentrations. These measures can also be assumed for varying particle sizes. Particles can be suspended in the air for long periods of time. Total suspended particulate (TSP) matter includes particles of all sizes. A significant fraction of TSP consists of particles too large in size to enter the human respiratory tract.

According to the explanation of CPCB of India, the main goal of air quality control is "to control pollution within the levels at which harmful effects on human health can be minimized, paying particular attention to ecologically sensitive areas (notified by central government) and the environment as a whole" (CPCB 2009). The air quality research in general focuses on particles those can cause damage to human health. This further insists on acquiring knowledge about 'how deep particles can penetrate into the human lung'. Particles smaller than 10μm can pass the nose and penetrate into the pharynx or throat (Herbarth 1998). Furthermore, particles in the range of 2–3μm can reach the lower part of the respiratory airways, and finally, the remaining particles can penetrate into the terminal bronchioles and alveoli. The Fig. 1.1 shows typical particulate penetration in the human respiratory system. In Fig. 1.1, Inhalable Particulate Matter (IPM) represent all particles that enter the human respiratory tract and Thoracic Particulate Matter (TPM) represents particles that travel past the Larynx and reach the gas exchange region of the Lungs.

In measuring respirable particulate matter (RPM) of ambient air, air quality researchers use mainly mass concentrations of particles belonging to different size fractions. These are abbreviated as PM_x, with PM meaning "particulate matter" and x referring to the

respective aerodynamic diameter. For example, PM_{10} is defined as "size convention that closely resembles the thoracic size distribution (Fig. 1.1) and has a 50 percent penetration at 10-micron equivalent diameter/aerodynamic diameter" (IS5182 2006).

Since most particles are irregularly shaped, the determination of their diameter is based on the concept of aerodynamic diameter. The aerodynamic diameter means the diameter of a sphere of density $1 g/cm^3$ which shows the same terminal settling velocity in calm or laminar flowing air as the measured particle.

1.2.1 SOURCES OF PARTICULATE MATTER

In urban agglomerations of industrialized countries, a variety of point and line sources of particles can be found whereas industrial activities including power generation and domestic heating with coal or oil are point sources. Emission of particles from motorized traffic occurs mainly along roads and hence constitutes a moving point source. Emissions by motorized vehicles do not only include exhaust particles but also abrasion products from tyres, brakes, clutches, and the road's surface. Furthermore, particles are emitted by resuspension of previously deposited particles by vehicle-induced turbulence. Besides the local emissions, particle concentrations in cities are also influenced by advection due to particle transport from rural surroundings or long-range, often trans-boundary transport.

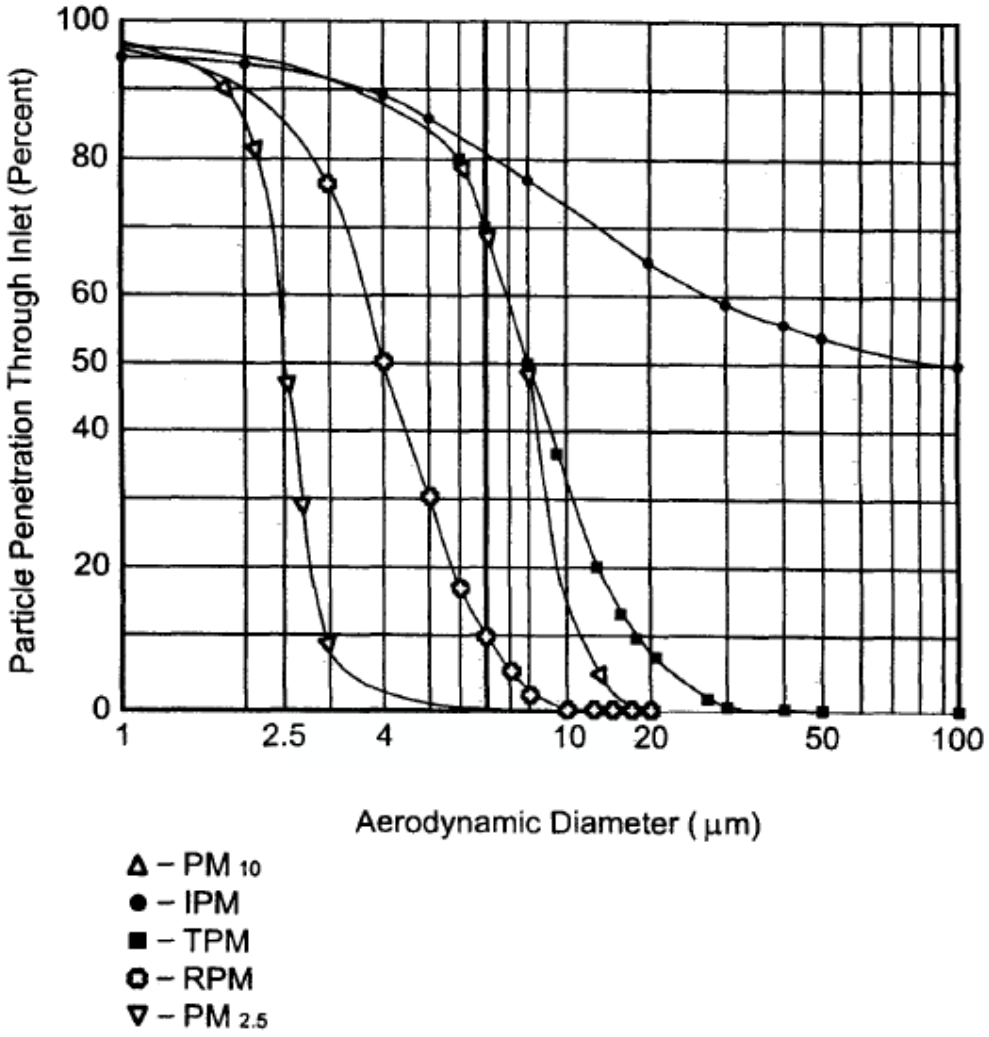


Figure 1.1. Size distribution of particulate penetration in different positions of the human respiratory tract. (Taken from Indian Standard IS 5182 (Part 23):2006)

The ultrafine particles of size range less than 0.1 μm are formed by nucleation i.e., condensation of low vapor pressure substances formed by high temperature vaporization or by chemical reactions in the atmosphere to form new particles (nuclei). They are mainly of anthropogenic origins such as from automobile exhaust, wood smoke and emission from diesel engines and generators (Kleeman et al. 1999; Lippmann 1998; Shi et al. 1999). Fine particles of size range 0.7–1.0 μm are formed by accumulation or coagulation of ultrafine particles. In close vicinity of the road, the contribution of traffic to fine particle concentration

was 58–68% (Wróbel et al. 2000). Biomass burning is another important source of fine organic aerosols (Simoneit and Elias 2000). Coarse particles ranging from 1 to 200 μm are predominantly rock or soil material of natural origin emitted into the atmosphere by mechanical grinding or spraying. These particles can include windblown dust from agricultural processes, uncovered soil, unpaved roads or mining operations. Traffic produces road dust and air turbulence that can re-entrain road dust. Near the coast, evaporation of sea spray can produce copious particles. In the urban atmosphere, dust arises due to the agitation of soil through activities such as vehicular movement, construction and earth moving (Gamble 1998; Miranda et al. 1999). An estimated 80% of coarse particles from traffic in the urban environment settles within 150 m distance from the road, ~40% at 200–270 m, and ~20% at about 1500 m (Wróbel et al. 2000). PM_{10} fraction is mainly dominated by particles from three sources: (i) Primary fine PM from industrial and combustion sources, predominantly road traffic. (ii) Secondary aerosol, mostly ammonium sulphate and ammonium nitrate formed through photochemical reactions. (iii) Windblown soil and resuspended street dust present largely in coarse fraction (2.5–10 μm) (Harrison et al. 1997). In India, the coarse particles make a significant contribution to the particle mass, with coarse particles showing seasonal variation from about 20% of the total PM_{10} mass in winter to 50% in summer, reflecting the impact of drier summer climate on the re-suspension process. In the urban atmosphere, it is found re-suspension of paved road dust contributing up to 25–63% of the PM_{10} (Lippmann 2000).

1.2.2 Environmental and Health Effects of Particulate Matter

Like most of the environmental problems, the effect of air particulate matter is also very complex in nature. As discussed earlier, particulate matter contains a mixture of directly emitted particles and indirectly (secondary) formed particles from the chemical transformation of gaseous pollutants. Soil related particles and organic/elemental carbon

related particles from combustion process are the principle categories of directly emitted particulate matter. The secondary particles are mainly the result of the reaction between ammonia and SO_2/NO_x forming sulfates and nitrates. Besides the effects of these primary and secondary particles, some components of particulate matter react with other particles to produce byproducts that have significant consequences for the environment. One of those significant consequences is destruction of tropospheric ozone. Main environmental effects of particulate matter include acid deposition, impaired visibility and depletion of ozone. Reducing the particulate matter can clearly improve visibility and also can increase the ozone levels. The effects of reduction in PM concentrations on acid deposition are not clear. Another significant and detrimental effect of particulate pollution is the soiling of manmade surfaces. Acid deposition caused due to PM concentrations can cause some of the following effect on aquatic ecosystems: a) Bicarbonate anion decreases, which causes a reduction in acid neutralizing capacity b) Base cations (calcium, magnesium, sodium, potassium) increase, which prevent or minimize acidification of drainage waters, but may deplete soil reserves and affect forest growth c) Hydrogen cation increases (decrease pH), which can adversely affect aquatic biota d) Aluminum cation increases which can negatively affect aquatic organisms (Bhattacharjee et al. 1999).

Health impacts of air pollution are generally assessed by linking the concentration of air pollutants to the observed health effects. Particulate matter when present in high concentrations can cause adverse effects on human health (Hoek et al. 2002). Increased mortality from both respiratory and cardiovascular diseases have been epidemiologically linked to long term exposure to this type of pollution (Abbey et al. 1999; Dockery et al. 1993; Pope et al. 2002). Cardiovascular deaths, myocardial infarctions and ventricular fibrillation have been associated with exposure of particulate matter (Dockery 2001).

1.3 NEED OF MONITORING AND MODELING

PM pollution monitoring, modeling and management help to gain a deeper understanding of environmental processes and techniques for managing environmental changes. Air quality is a dynamic and complex environmental phenomenon exhibiting significant temporal and spatial variations. Acute PM pollution is being faced in urban agglomeration due to rapid economic expansion, an increase in population, increased industrial activities and exponential growth in automobiles. PM pollution can threaten the health of human beings, trees, lakes, crops and animals, ecology and property. In an attempt to manage urban air resources, it is necessary to have reliable information on the ambient PM concentrations in various activity zones of urban growth centers.

The improvement of air quality in an urban area in general constitutes of two phases, monitoring and modeling. A positive approach for monitoring and modeling is needed to identify major sources of PM pollution and subsequently restore air quality by corrective measures. PM pollution monitoring includes continuous monitoring of air quality parameters which include both PM pollution as well as meteorological parameters that influence the distribution of particulate matter. PM pollution monitoring gives valuable quantitative information about ambient concentrations and deposition, but they can only describe air quality at specific locations and times, without providing clear guidance on the identification of the causes of the problem. PM pollution modeling, instead, can provide a complete deterministic description of the air quality problem, including an analysis of factors and causes (emission sources, meteorological processes, and physical and chemical changes), and some guidance on the implementation of mitigation measures (Daly and Zannetti 2007). Air pollution models play a major role in PM pollution control because of their capability to assess the relative significance of different sources. Air pollution models are the only method that quantifies the deterministic relationship between PM emissions and their

concentrations/depositions. Those relationships include consequences of the past and future scenarios and determining the effectiveness of abatement strategies which makes air pollution models indispensable in regulatory, research and forensic applications.

1.4 AIR POLLUTION MODELS

The essence of air pollution modeling, in general, is to capture the important aspects of the physical reality while discarding irrelevant details. It may therefore often be possible to devise several types of models of the same physical reality. One can pick and choose among these depending on the desired model accuracy and their capability of analyzing the air quality. It is important in this respect recognizing the fact that most mathematical models are not completely based on rigorous mathematical formulation of the physical and chemical processes taking place in the atmosphere. Every mathematical model contains a certain degree of empiricism. The degree of empiricism limits the generality of the model and, as our knowledge of the fundamentals of the atmosphere increases, the degree of empiricism decreases and the generality of the model increases. Models always contain certain simplifying assumptions which are believed; not to affect the nature of the model in any manner that undermines the purpose of it. The distribution, dispersion and transformation of particulate matter in ambient air are the processes whose physics and chemistry are poorly known. For modeling such process a different approach is followed called 'Data Based Modeling' or 'Black Box Modeling' or 'empirical modeling'(Kavuri 2011). Here the modeling will be done based only on empiricism. In this context, air pollution modeling can be divided into two categories.

1.4.1 DISPERSION MODELS

Mathematical simulation of pollutant emissions and their transportation throughout the atmosphere is considered as dispersion modeling. In dispersion modeling, atmospheric

conditions (like mixing height, wind speed and direction and air temperature, etc.) are replicated to provide an estimate of the concentration of pollutants during their travel in the atmosphere from an emission source (Holmes and Morawska 2006). If one can incorporate atmospheric chemistry in it, a dispersion model can also generate approximations of secondary formation of PM pollution. Generally in cases like allowing a new source in the current region or prediction of beneficial effects of controlling a particular source, the dispersion models are highly recommended.

The complexity of dispersion models ranges from very simple to highly complicated models. The minimum requirements for any dispersion model will be meteorological data, emissions data, and details about the facilities in question (such as stack height, gas exit velocity, etc). When the complexity of the models increases the requirement may expand to topography information, individual chemical characteristics and land use data. The output from this type of model is a prediction of the concentration of the pollutant in question throughout the appropriate region (which depends on the model chosen). For example Buoyant line and point source (BLP) dispersion model is recommended for rural areas with transport distances less than 30 km, simple terrain, and averaging times less than one year, whereas Complex Terrain Dispersion Model Plus (CTDMPLUS) is recommended for complex terrain, elevated point sources, transport less than 50 km, rural or urban areas, and averaging times up to one year.

1.4.2 DATA BASED MODELS

Data-based models are data dependent and ambient air pollution data determines the model parameters. Hence these models are called data-based models. Unlike the dispersion models derived from first principles, the data based models or empirical models do not describe the mechanistic phenomena of the process; they are based on input-output data and only describing the overall behavior of the atmosphere. The data based models were particularly

appropriate for problems that are data rich, but hypothesis and/or information poor (Kavuri 2011). In all the cases the availability of a sufficient number of air quality data is required to propose a good model. Quality data is defined by noise free data; free of outliers is ensured by data mining and pre conditioning. Two main types of data based models exist.

1.4.2.1 RECEPTOR MODELS

Receptor modeling is the application of multivariate statistical methods addressed to identification and quantitative apportionment of air pollutants to their sources (Hopke et al. 2006). Receptor-based models use chemical characterization data at an individual observing site (the receptor) to compute the relative contributions from significant sources to the pollution at that site. Receptor-based modeling is likewise alluded to as source apportionment. These models can be applied to explore different individual “air pollution episodes" or, as with the emission inventory, to make successful control systems. Receptor-based models are most usually used to identify and quantify the sources of particulate matter, utilizing speciated chemical characterizations data of the sampled particulate matter.

The primary inputs for receptor models are chemical characterizations data at a receptor. These are typically acquired by gathering particulate matter on a filter and breaking down the filter for the chemical components and organic carbon. The Chemical Mass Balance (CMB) model requires the further contributions of the uncertainty connected with every measurement and the source emission profiles. A source profile is the chemical characterization of the emissions, with every species reported as a mass fraction of the aggregate (for instance, resuspended dust may contain 20% aluminum, 20% calcium, 50% silicon, and 10% elemental carbon). Some advanced models like Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA), don't require source profiles as an input, as the solution itself contains these profiles.

The primary yield from these models is an assessment of the contributions from every source to the air pollution at that site. From an administration point of view, the outcomes from these models are vital for logically justifying priorities and observing patterns.

1.4.2.2 AIR QUALITY FORECAST MODELS

Air quality forecast models try to find out the association between specific meteorological parameters and air quality can be quantified using a variety of statistical techniques. These air quality forecast systems can supplement the existing emission control programs in a remarkable way. In many parts, the air quality standards are exceeded frequently in a year (Kumar and Goyal 2011). The availability of reliable air pollution forecasts affords local environmental regulators the option of "on demand" or intermittent emission reductions on those days, thus avoiding the high cost of continuous emission control. This approach is currently being successfully employed in several countries and could be expanded were reliable forecasts available.

The most common techniques in use for air pollution forecasting are:

- Classification and Regression Tree (CART) – This technique uses specialized software to identify those variables (meteorological or air quality) that are most strongly correlated with ambient pollution levels. These variables are then used to predict future pollution levels based on current air quality and forecasted meteorology.
- Regression analysis – The association between pollutant levels and meteorological and aerometric variables can be quantified by analyzing historical data sets using standard statistical analysis packages. The resultant multi-variant linear regression equation can be used to forecast future pollution levels.
- Artificial Neural Networks – Another way of analyzing historical data is to identify atmospheric parameters that influence air quality and quantify that association

through the application of adaptive learning and pattern recognition techniques, such as neural networks. Neural networks are intended to mimic the way the human brain recognizes recurring patterns. ANN is found to be superior as they can determine linear, non-linear and also complex relations between the parameters.

1.5 SOURCE APPORTIONMENT AND RECEPTOR MODELING IN INDIA

In India, air pollution is gradually becoming a dangerous risk to the environment and quality of life amongst the urban population because of the enormous amounts of urbanization. In Indian scenario, particulate matter is reported to be consisting of various metals including Ni, Cu, Zn, Pb and Cr indicating the dominance of anthropogenic sources (Negi et al. 2002b; Prati et al. 2000; Rastogi and Sarin 2009). National Ambient Air Quality Standards (NAAQS) were regularly exceeded despite increasing efforts on PM emission control in recent years. The major causes of air pollution in India have been identified as industrial emissions, biomass burning, vehicular emissions, coal combustion, road dust and refuse burning (Pant and Harrison 2012).

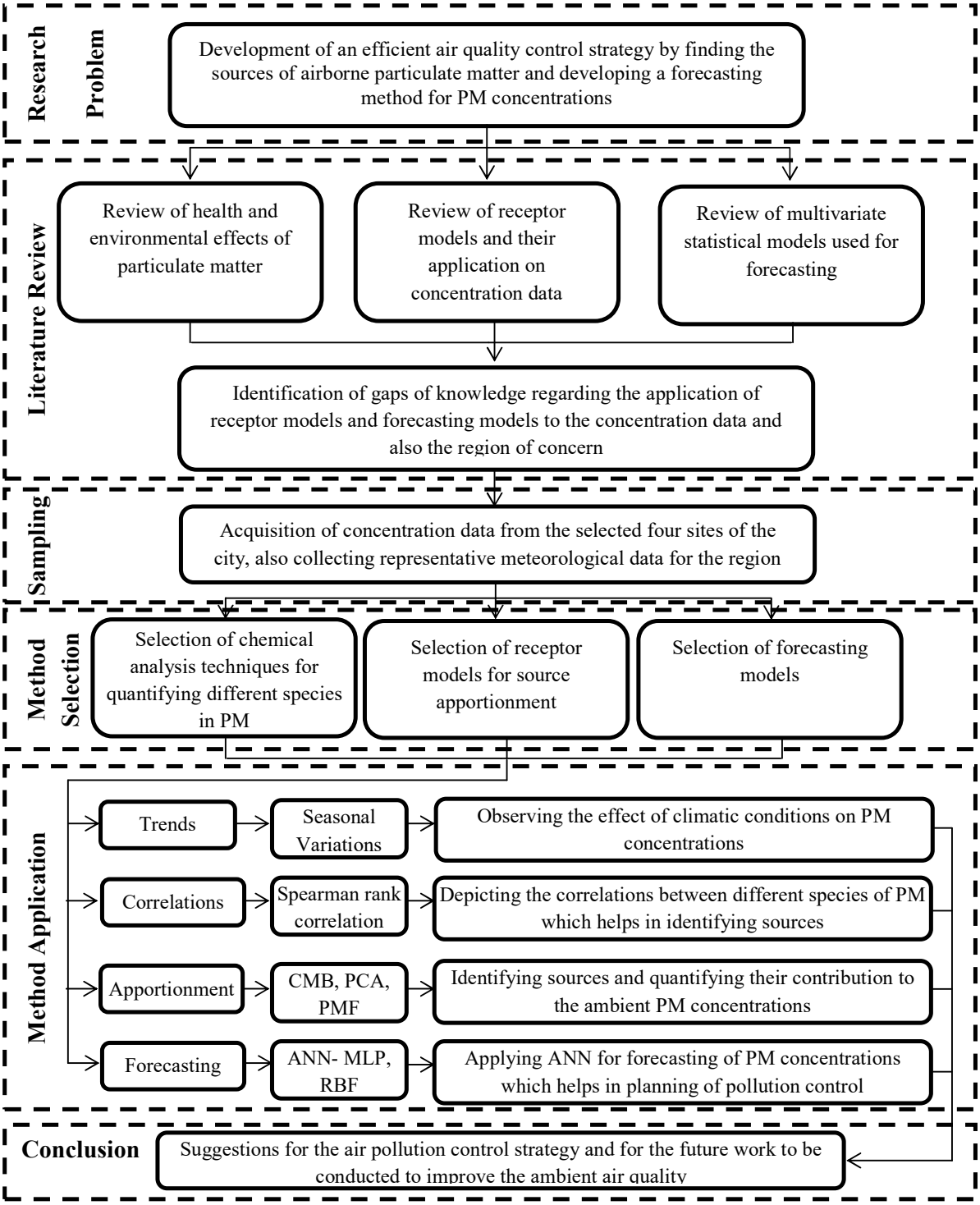
Source apportionment of PM in India using receptor modeling has a increasing figure of literature in recent years. A bulk of the source apportionment studies have been conducted using multivariate approach; principal component analysis (PCA) being the most frequently used technique but there are some cases of application of the chemical mass balance (CMB) model (Gupta et al., 2007; Srivastava et al., 2005). As discussed earlier, CMB model requires the additional input of source emission profiles which can be one of the explanations for use of multivariate models (which does not require source profiles). Most of the studies using CMB have to use the source profiles available through USEPA SPECIATE database which

may not represent the Indian scenario appropriately. In the recent times there is an effort gone to generate source profiles for some of the sources in India (Patil et al., 2013).

1.6 SCOPE OF THE WORK

- To successfully assess the PM air pollution in Rourkela that can help in preparing a strategy for mitigating major sources.
- To find the relation between meteorological parameters and PM pollution at the receptor site which helps in developing a real time forecasting mechanism.
- To give a pathway to follow in setting up an Urban Air Quality Management Programme (UAQMP) for Rourkela and other steel cities.

RESEARCH STRATAGY



CHAPTER 2- LITERATURE REVIEW

2 LITERATURE REVIEW

Air pollution has become a major concern worldwide as it adversely affects human health and environment. In 2012, an estimation of approximately 3.7 million premature deaths worldwide per year has been attributed to increased air pollution levels (WHO 2014). Along with adverse health effect, air pollution also contributes to tremendous economic losses, especially in the matter of financial resources for providing medical assistance to affected people. Economic growth and increasing urbanization in India are accompanied by a rise in ambient air pollution levels, especially in urban areas (Ghosh and Mukherji 2014). The effects of air pollution are very complex as the individual effects from different sources vary considerably. Hence, monitoring of various pollutant parameters becomes essential for proper assessment and evaluation air quality. The data generated from monitoring of air quality can be used to verify compliance with local and national air quality standards and for forecasting purposes which further supports in the development of regulations for the air quality control. It also helps in the assessment of the effectiveness of contemporary air pollution control programs. The monitoring data will also be helpful in apportioning the pollution contributions to various sources contributing at local level. The present study devotes special attention to the following aspects:

2.1 AIR POLLUTION HISTORY

The 20th century began with the developed nations of the world several decades into the industrial revolution. They were rapidly getting away from thousands of years when most

physical work was done by muscle power, both human and animal. Steam power, produced by burning various fuels, was replacing muscle power and providing much greater amounts of energy for numerous purposes. Many industries used this energy to provide manufactured goods that added to the quality of life and improved standards of living, at a fraction of the previous costs. Transportation had also changed significantly, with steam driven rail roads and steamships replacing sailing ships and land transportation by horses to move people and goods. The first few decades of the 20th century saw significant progress that continued developments begun during the latter decades of the 19th century. This was quickly evident in the growing use of internal combustion engines for transportation and electric motors for stationary applications.

Prior to the 20th century, air pollution complaints were few and attempts to control it were scattered and largely ineffective. Air pollution was usually tolerated in order to obtain the many advantages that were available through the increased use of energy. But rapid growth in fuel consumption during the early part of the 20th century began to cause more serious problems, especially in the highly populated cities of the developed countries, where coal was the most abundant and cheapest fuel. Complaints became too numerous to be ignored, so control efforts were increased. Air pollution control in the first half of 20th century can best be described as the era of the Ringelmann Chart, which was developed and became a standard in the ASME Power Test Code during the 1890s (Anon 1952; Ringelmann 1898). As illustrated in Figure 2.1, it was a white chart with five gray squares that were successively darker shades of gray, numbered 0 through 5. It was used as a guide in making visual estimates of the density of smoke coming out of a stack.

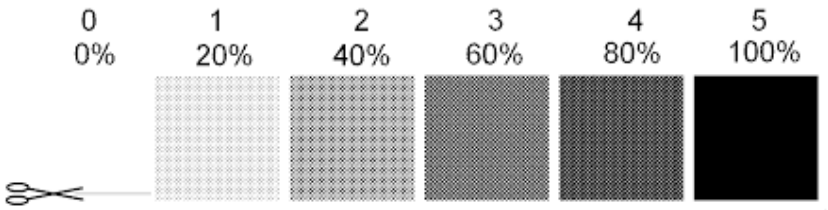


Figure 2.1. Ringelmann chart with gray squares

This was the most sophisticated air pollution measuring device of its time, and it was used extensively even into the second half of the 20th century. It worked well, at a time when smoke and soot in the coal burning areas of the nation caused most of the air pollution complaints. Smoke inspectors, usually working for local governments, enforced ordinances that prohibited smoke "darker than Ringelmann No. 2" or some comparable limitation. While the Ringelmann chart and the work of the smoke inspectors seem primitive by today's standards, they made things a little easier for housewives who often had to put up with black soot and other particulate matter falling on their laundry while it hung outside to dry. People who developed and operated local government programs were also the pioneers who established a basis for the more comprehensive and effective control programs that came later. In 1907, some of these smoke inspectors formed a professional organization called the International Association for the Prevention of Smoke the original predecessor of the Air & Waste Management Association (AWMA)(England, 1999).

The following events were among the most important that marked the dividing line between air pollution control in the first and second halves of 20th century:

- ✓ Two air pollution episodes in Donora, PA (1948) and London (1952), caused many people to become ill and a significant number died. These health effects were attributed to the same pollutants that were present in those localities every day but which became lethal when they accumulated during prolonged periods of stagnant air.
- ✓ In 1952, a scientific paper by A J. Haagen-Smit of CalTech identified the reaction mechanism responsible for the familiar but little understood Los Angeles smog problem,

identified ozone as a characteristic byproduct, and for the first time, provided data that pointed to motor vehicles as a major cause of air pollution (Haagen-Smit 1952).

Those episodes and the deaths they caused created public concern. Suddenly, air pollution was much more than just a nuisance. Haagen-Smit's paper didn't attract much attention, but among the scientists who were concerned about this mysterious problem, it soon became clear that this paper had cleared up a lot of the mystery and that photochemical smog and ozone represented a very complex problem that would be difficult to solve.

These events and changes began what might be termed the hightech era of air pollution control, which continues today. The Ringelmann chart soon was supplemented by sophisticated measurement methods and instruments, detailed meteorological studies, monitoring networks, laboratory chambers to duplicate the photochemical reactions involved in ozone formation, and all of the other scientific and technological activities familiar today. These technological developments were not created in a vacuum, just to study air pollution problems. Science and technology began expanding at an ever increasing pace after World War II, triggering massive changes in all segments of our society. This rapid growth of science and technology affected the high-tech era of air pollution control as soon as it began and, if anything, even the rate of change has increased. It would take a book to present just a bare outline of the changes over the past 50 years. Instead, only a few major advancements will be mentioned; many will have their own different list from those mentioned here.

- ✓ One of the greatest changes has been in the measurement of air contaminants. Around the middle of the century, ambient air measurements were usually performed manually, measuring a few common contaminants at concentrations in the parts per million ranges. Now, modern instruments and technology make it possible to measure dozens of individual constituents in a single sample. Results in parts per billion (ppb) are routine

and in parts per trillion are not unusual. Overall, selectivity is far better and limits of detection for many contaminants have been reduced by four to six orders of magnitude.

- ✓ Satellite technology is providing meteorological and air quality data that are a valuable addition to data obtained with aircraft and ground based equipment. Two examples include (1) visual and radar information that helps in understanding meteorological factors that affect air pollution on both continental and worldwide scales, and (2) atmospheric temperature and other measurements from space that can cover the entire earth in a short time, whereas ground based measurements are severely limited because of the scarcity of observations over the oceans, which cover about three-fourths of the earth's surface.
- ✓ Computer technology has had tremendous effects on most activities, starting with mainframes in the 1950s and expanding with microcomputers since the 1970s. Air pollution control is no exception. Many jobs are now done more easily and better as a result: calculations, data logging and analysis, process control, multipurpose computer modeling, obtaining information from the Internet, and many others.
- ✓ Laws and legal standards have also been through tremendous changes. Instead of local problems monitored by local governments, coordinated regional and inter-state programs were developed to deal with more complex and widespread problems.

The most important sign of this progress is that urban monitoring networks show consistent reductions in measured levels of pollution. Many areas can demonstrate significant progress toward achievement of the National Ambient Air Quality Standards (NAAQS). Unfortunately, they still have a long way to go. But the lack of complete success should not prevent from recognizing the significant progress that has been made. Perhaps most important for the future, a comprehensive system of programs and organizations is in place that safeguard air quality and resolve related health concerns. That system includes

comprehensive laws and regulations; government agencies; skilled professionals in many different fields, working in both the public and private sectors; university programs, to train the next generation of professionals; control technology, to reduce emissions from numerous industrial operations; and motor vehicles. Improvements are still needed and are being developed.

2.2 AMBIENT URBAN AIR POLLUTION

In developed countries, reverse trends of urbanization and its associated growth of cities have started because of austere levels of congregation (Mayer 1999), whereas urbanization in developing countries tends to be increasing from periphery to core. Ambient air pollution levels at urban hot spots in 20 European cities have exceeded the urban background concentrations due to increase in traffic volume (Moussiopoulos et al. 2005). In the UK, motorized road transport has been categorized as one of the largest single pollution sources in 92% of declared air quality management areas (AQMAs) which accounts for 21% of PM_{10}, and so, frequently violating the national ambient air quality standards (Faulkner and Russell 2010). However, in the recent past, it has been observed that in some mega cities of developed countries, urban air quality is showing signs of improvement on account of efficient implementation of urban air quality management plan (UAQMP) (EEA 2011, 2013; NSW 2010; Parrish et al. 2011).

The developed countries of Asian subcontinent such as Singapore, Japan and Hong Kong, are facing street level air pollution problems due to increased motor-powered transportation (ADB 2006; Edesess 2011). In developing countries, mega cities are facing acute problems due to an increase in the ambient PM and NO_2 concentrations as a result of rapid urbanization. In Shanghai, New Delhi, Mumbai, Guangzhou, Chongqing, Calcutta, Beijing, and Bangkok the ambient PM and NO_2 concentrations frequently violate WHO

guidelines (Baldasano et al. 2003). The major causes of deteriorating urban air quality in developing countries are found to be (Badami 2005; Gurjar et al. 2004) poor fuel quality, high traffic density, large proportion of old vehicles, poor road infrastructure and inadequate inspection and maintenance (I/M) programs.

Chan and Yao (2008) have reported that four to six folds higher ambient concentrations of PM_{10} and SO_2 were observed in the Chinese cities of Shanghai and Pearl River Delta compared to the cities in developed countries. In Beijing, the annual average NO_2 concentrations remain constant at a level of 70μg/m^3 ±10%. However, 90% of the time, PM concentrations exceed the NAAQS and WHO–AQG (Duan et al. 2006; Zheng et al. 2005).One of the studies carried out recently has found that the annual average PM_{10} concentrations in Asian cities are four times higher than WHO's air quality guidelines of 20μg/m^3 (Atash 2007; CAI-Asia 2010; United-Nations 2011).

In the Indian metropolitan cities (Delhi, Mumbai, Kolkata and Chennai), ambient PM concentrations frequently violate National Ambient Air Quality Standards (NAAQS) as well as WHO guidelines (CPCB 2010; Gupta et al. 2010; Gupta and Kumar 2006; Singh et al. 2007). Mohan and Kandya (2007) have analyzed nine years of data at seven different locations in the city of Delhi and reported that at one of the locations (ITO intersection), the air quality has been found to be "worst". Gurjar et al. (2008) have developed a multi-pollutant index for 18 megacities of the world, out of which, five are classified as "fair" and thirteen as "poor". Further, Ramachandra (2009) has reported that India's transport sector emits 258.10Tg of CO_2, of which 94.5% is contributed by motor-powered transportation.

The Central Pollution Control Board (CPCB) has reported that vehicular contribution to the total urban air pollution in Delhi and Mumbai is about 76–90% for CO, 66–74% for NO_X, 5–12% for SO_2 and 3–12% for PM (CPCB 2010). Recently, studies carried out by Yale University, USA, and WHO, have ranked Delhi as the "worst" polluted city based on

environment performance index (TOI 2014). Therefore, necessary mitigation measures need to be implemented through effective and efficient implementation of urban air quality management plan (UAQMP) to maintain an acceptable urban air quality.

2.3 AIR QUALITY MONITORING

Information regarding the present status of air quality is provided by air quality monitoring, further helping in evaluation of current guidelines and their operational execution. Planning, design and establishment of monitoring network according to the objectives is one of the key apparatus of any air quality monitoring (Sivertsen 2008). In 1981, a monitoring network was designed in Fulton County, Georgia, to monitor only nonreactive pollutants in ambient air (Graves et al. 1981). Some air quality monitoring networks like Greater London area has an objective to specifically carry out spatial correlation analysis using the data obtained from the monitoring stations (Handscombe and Elsom 1982). In recent years, multiple-objective approach has been chosen to design an otrimal air quality monitoring network in Riyadh City, Saudi Arabia (Mofarrah and Husain 2010).

Monitoring network in USA is designed and operated according to the guidelines of Office of Air Quality Planning and Standards. Monitoring network data are analyzed to forecast air quality index (AQI) in over300 cities (www.airnow.com). Over 300 air quality monitoring stations are operated in UK (DEFRA 2016). There are provisions for obtaining real time hourly average air quality information through electronic media and web platforms. Administration of monitoring netwoks in EU coountries is done through European Topic Centre on Air Pollution and Climate Change (EEA 2016).

In most of the developing countries, the air quality monitoring network has been designed primarily to ensure effective regulatory compliance. China National Environmental Monitoring Center operates and maintens the air quality monitoring stations in 113cities with

more than 2000 stations in China (CNEMC 2016). South Africa has 94 air quality monitoring stations operated all over the country (DEA 2011). In Hong Kong, There are 14 online continuous monitoring stations in Hong Kong maintained by Environment Protection Department (EPD, 2011). Yet, the Pearl River Delta regional air quality monitoring network serves as a role model for cooperation between the two governments and among various local authorities to address the air pollution problems in a more effective and holistic manner (Zhong et al. 2013). National Air Quality Monitoring Programme (NAMP) network in India has 342 monitoring stations in 127 cities/towns in 26 states and 4 union territories. Additionally, individual state pollution control boards are operating their own monitoring stations (CPCB 2016). Under N.A.M.P., four air pollutants viz ., Sulphur Dioxide (SO_2), Oxides of Nitrogen as NO_2, Totla Suspended Particulate Matter (TSP) and Respirable Suspended Particulate Matter (RSPM / PM_{10}) have been identified for regular monitoring at all the locations. The monitoring of meteorological parameters such as wind speed and wind direction, relative humidity (RH) and temperature were also integrated with the monitoring of air quality. The monitoring of pollutants is carried out for 24 hours (4-hourly sampling for gaseous pollutants and 8-hourly sampling for particulate matter) with a frequency of twice a week, to have one hundred and four (104) observations in a year (CPCB 2016). The monitoring is being carried out with the help of Central Pollution Control Board; State Pollution Control Boards; Pollution Control Committees; National Environmental Engineering Research Institute (NEERI), Nagpur. CPCB co-ordinates with these agencies to ensure the uniformity, consistency of air quality data and provides technical and financial support to them for operating the monitoring stations. In the recent past, the Ministry of Earth Sciences (MOES), Government of India has started monitoring of criteria air pollutants, specifically designed for Delhi City and operated by the Indian Institute of Tropical Meteorology (IITM), Pune (IITM,2014). Now MOES initiated a monitoring network called

System of Air Quality and Weather Forecasting And Research (SAFAR). The SAFAR observational network of Air Quality Monitoring Stations (AQMS) and Automatic Weather Stations (AWS) established within city limits represents selected microenvironments of the city including industrial, residential, background/ cleaner, urban complex, agricultural zones etc. as per international guidelines which ensures the true representation of city environment. Air Quality indicators are monitored at about 3 m height from the ground with online sophisticated instruments. These instruments are operated round the clock and data is recorded and stored at every 5 minute interval for quality check and further analysis. Pollutants monitored include PM_1, $PM_{2.5}$, PM_{10}, Ozone, CO, NO_x (NO, NO_2), SO_2, BC, Methane (CH_4), Non-methane hydrocarbons (NMHC), VOC's, Benzene, Mercury. Monitored Meteorological Parameters include UV Radiation, Rainfall, Temperature, Humidity, Wind speed, Wind direction, solar radiation. This is the first of such kind of network in India which continuously monitors all these parameters and maintain up to date data base with robust quality control and quality assurance. IITM has collaborated with different institutes/organizations who have extended their full cooperation and support by providing the infrastructure and other facilities to establish SAFAR network. There are four SAFAR observational networks namely Ahmedabad, Mumbai, Pune and Delhi with each network consisting of Ten cities to be monitored.

2.4 SOURCE APPORTIONMENT

Source apportionment (SA) studies are conducted to identify and quantify sources that pollute a receptor site. An efficient and effective UAQMP needs input on categories of sources that may contribute to ambient air pollution followed by their quantification. Based on this information, effective UAQM strategies can be formulated and implemented. The SA studies can be performed using methods that rely on an analysis of morphological and

chemical composition of pollutants. The latter, being the quantitative technique, is preferred over the former one for use in large scale studies. Chemical characterization, thus, is an important step in the SA studies that focuses on obtaining chemical constituents of the PM, which depend on sources and their emission rates. To apportion the sources, receptor models are used, which quantify pollutant concentrations based on the measured ambient air pollutant data. SA studies using receptor models date back to late 1960's, with the first study reported in literature by Blifford & Meeker (1967). They have examined particle composition data of TSP collected by the National Air Sampling Network (NASN) during 1957–61 in 30 U.S. cities using factor analysis and eigenvector method for 13 elements. Very few studies have been conducted nation–wide (CPCB 2010; Thurston et al. 1984, 2011); majority of the studies have been conducted only on regional and local scales (Ito et al. 2004; Qin et al. 2006; Tao et al. 2013).

However, the focus of these studies has been shifting from coarser particles (TSP, PM_{10}) to finer particles ($PM_{2.5}$, PM_1) that significantly affect health (Chakraborty and Gupta 2010a; Khare and Baruah 2010a; Mazzera et al. 2001; Pandolfi et al. 2011; Schauer and Cass 2000). One of the important parameters in SA studies is the selection of marker species or source profiles. Metals have been used invariably as marker species for identification of sources for instance, Al, Si, Ti, Ca for crustal/soil sources; Ni, V for residual/fuel oil combustion; Zn, Cr for refuse burning/incineration; and Zn, Cr, Pb, Cu for vehicular emissions (Chow et al. 2011; Patil et al. 2013b; Watson et al. 2002). The ratio between two metal concentrations represents the characteristic of a particular source which is an important input for receptor models. Besides, an efficient and effective UAQMP requires specific information on emission sources which may be categorized based on the type of fuel used. In order to identify such sources, organic molecular markers are used as tracers along with metals, ions and EC/OC (Li et al. 2014; Perrone et al. 2012; Schauer et al. 1996). These

markers have a high degree of source specificity; for instance, levo glucosan from cellulose has been used as a specific marker compound for wood burning; hopane and stearanes for mobile source emissions; and polycyclic aromatic hydrocarbon (PAH) profiles for distinguishing between gasoline and diesel vehicle emissions (Chowdhury et al. 2007; Herlekar et al. 2012; Lin et al. 2010; Masih et al. 2010; Sharma et al. 2003; Simoneit et al. 1999). Hasheminassab et al. (2013) have used molecular marker–based chemical mass balance model (MM–CMB), which possesses higher source identification efficiency when compared to CMB, which is one of the most widely used receptor models (Watson et al. 2002, 2008). Other receptor modeling techniques used in SA studies include enrichment factor analysis, time-series analysis, multi variate factor analysis (principal component analysis and positive matrix factorization), UNMIX, species series analysis and multi–linear engine (ME) analysis (Almeida et al. 2006; Begum et al. 2010, 2011; Bove et al. 2014; Cheung et al. 2011; Cooper and Watson 1980; Daher et al. 2013; Gietl and Klemm 2009; Henry et al. 1984; Hwang et al. 2008; Kertész et al. 2010; Kuo et al. 2014; Oliveira et al. 2010; Pakbin et al. 2011; Ramadan et al. 2003; Stone et al. 2010; Tecer et al. 2012; Viana et al. 2008; Watson et al. 1991). However, few SA studies have also been carried out using dispersion modeling approach (Colvile et al. 2003; Laupsa et al. 2009). Recent studies carried out in some of the urban areas in USA have concluded that metal/steel industries, motor exhaust and crustal emissions are major contributors of $PM_{2.5}$ and PM_{10} concentrations in ambient air (Coûtant et al. 2003; Green et al. 2013; Hasheminassab et al. 2013; Sturtz et al. 2014; Thurston et al. 2011). Studies conducted in European urban cities, motorized transport, crustal sources and mixed industrial/fuel oil combustion are major sources of $PM_{2.5}$ and PM_{10} (Belis et al. 2013; Viana et al. 2008; Yin et al. 2010).

Since the last decade, many developing countries have included SA as an important component of UAQMP. In China, several studies have been carried out focusing

identification, categorization and quantification of PM sources in ambient urban air and their correlation with human health (Breitner et al. 2011; Gu et al. 2010, 2011; Kong et al. 2010; Leitte et al. 2011; Liu et al. 2013; Song et al. 2006; Wang et al. 2013; Xie et al. 2008; Zhu et al. 2011). In South Africa, a few studies have been conducted on identification and quantification of source contributions to PM in urban ambient atmosphere (Beukes et al. 2014; Engelbrecht et al. 2002; Maenhaut et al. 1996; Piketh et al. 1999). In Brazil, source apportionment studies were mainly in urban areas like Rio de Janeiro (Godoy et al. 2009; Soluri et al. 2007), Capivari de Baixo (Godoy et al. 2005) and Cuiaba (Maenhaut, Fernandez-Jimenez, & Artaxo, 1999).

2.4.1 SOURCE APPORTION STUDIES IN INDIA

There is a growing body of literature on source apportionment of PM in India using receptor modeling. A majority of the SA studies have been conducted using multivariate methods; PCA being the most commonly used technique although there are some cases of application of the CMB model (Gummeneni et al. 2011; Gupta et al. 2007a; Karar and Gupta 2007). One of the key reasons for use of multivariate models is the absence of local source profiles, and it is only in the recent times that source profiles have been generated for some of the sources in India. Most of the studies using CMB have used the source profiles available through the USEPA SPECIATE database. Gupta et al. (2007) prepared soil dust and road dust source profiles for Kolkata, and the recently released Central Pollution Control Board (CPCB) source apportionment study (CPCB 2010) also contains India specific source profiles for a number of sources. Use of microscopic methods has also been reported though it has not been widely applied (Bandhu et al. 2000; Srivastava et al. 2009). Enrichment factor analysis has been used in several cases, either in conjunction with factor analysis or independently (Negi et al. 2002a; Shridhar et al. 2010). One study has been reported using PMF analysis (Bhanuprasad et al. 2008) although it was conducted at a regional scale (an Indian Ocean

cruise) rather than at the city level. There are only a couple of studies comparing results from different models, and in both cases, a comparison has been made between the CMB model and multivariate methods (Srivastava et al. 2009). Results of both the studies have indicated overall resemblance similar to other studies (Lee et al. 2008; Srivastava and Jain 2007).

Total suspended particulate matter (TSP) and PM_{10} have been studied in great detail due to concerns over the health impacts but in recent years, the smaller size fractions of particulate matter ($PM_{2.5}$ or less) have also gained immense importance given the recent evidence of their public health implications. However, much of the research is still focused on TSP and PM_{10}, with the exception of a few cases where $PM_{2.5}$ (Chowdhury et al. 2007; Gummeneni et al. 2011; Khare and Baruah 2010a) or PM_1 have been analyzed (Chakraborty and Gupta 2010a).

In terms of geographic distribution across the country, most of the studies have been conducted in New Delhi (Khillare et al. 2004; Shridhar et al. 2010; Srivastava and Jain 2007) followed by Mumbai (Chelani et al. 2008; Kothai et al. 2011; Kumar et al. 2001) and Kolkata (Karar et al. 2006; Karar and Gupta 2007). A few studies have been conducted in other cities including Kanpur (Chakraborty and Gupta 2010a), Chandigarh (Bandhu et al. 2000), Agra (Kulshrestha et al. 2009; Masih et al. 2010), Tirupati (Chandra Mouli et al. 2006) and Hyderabad (Gummeneni et al. 2011).

Out of all the literature, only Dhanbad is one such city which includes an integrated steel plant in its precincts where source apportionment has been conducted (Dubey et al. 2011). However, there are a limited number of analyses focused on measurement and analysis between urban and background locations (Chowdhury et al. 2007; Shridhar et al. 2010) where results have indicated significant enrichment of trace metals in the urban environment. A majority of the PM source apportionment studies have been conducted using trace element markers (Kothai et al. 2011; Kumar et al. 2001; Srivastava and Jain 2007) and

in some cases, inorganic tracers have been used in conjunction with organic and elemental carbon (Chelani et al. 2010; Tiwari et al. 2009). The use of organic molecular markers for PM source apportionment has only been reported in recent years (Chowdhury et al. 2007; Masih et al. 2010).

According to census of India 2011 it is estimated that over 46 cities will have a population more than one million by 2012 (it may have increased to 50 cities by 2016). In such case there is a strong need to extend the source apportionment studies to other cities with rapid population growth. Very few studies of source apportionment considering steel cities i.e an urban area in which a steel plant is an integrated part were reported. One such city with rapid growth in population and is so called steel city Rourkela is being considered for the present research to add to the knowledge.

2.4.2 PM POLLUTION FROM STEEL PLANTS

Epidemiological and toxicological investigations were sought to establish the chemical components primarily responsible for particle toxicity (Harrison and Yin 2000). Such studies have frequently implicated the metal content (particularly water-soluble metals like calcium, magnesium, sodium,) as a possible harmful component of particulate matter (PM), which triggers the generation of reactive oxygen species, switching on cellular pro-inflammatory response pathways (Adamson et al. 2000; Costa and Dreher 1997; Donaldson et al. 1997). The sources of particle-bound metals are vast, with metals such as aluminum, silicon, iron, and calcium arising from crustal materials, while heavy metals such as lead, cadmium, mercury, nickel, chromium, zinc, and manganese can be emitted from anthropogenic sources such as metallurgical processes and road transport (AQEG 2005; Birmili et al. 2006; Lough et al. 2005). The impact of steel plants on chemical composition of the PM has been investigated in a number of studies. Pope (1996) reported that, during the closure of a steel mill in the Utah valley, a reduction in PM_{10} mass and changes in its composition were

associated with decreases in morbidity and mortality of the local population. In a similar way, Hutchison et al. (2005) reported an increase in particle metal content when samples were taken downwind of a steelworks, which in turn were associated with an increased inflammation of a rat lung.

The integrated iron and steelmaking process is the main production route used in India and worldwide and is so-called because it involves a number of linked processes whereby iron is extracted from its ores in the blast furnace (BF) and the resulting molten iron is subsequently refined into liquid steel by the basic oxygen steelmaking (BOS) process. The integrated process also includes iron ore sintering and coke making facilities which are used to prepare agglomerated iron ores and coke, respectively, for use in the blast furnace burden. Emissions from integrated steelmaking facilities are a complex mixture of stationary source and fugitive emissions associated with the main processes, and fugitive emissions from general site operations such as the stocking, blending, and transportation of particulate raw materials on site. The situation is further complicated by the fact that some processes operate continuously while others are batch processes, some of which may be semi-continuous. Some of the main emission sources related to steel production, their characteristics and components of the emissions are summarized in Table 2.1.

Very few studies have endeavored to determine tracers for identifying impacts from steelworks, for example Oravisjärvi et al. (2003) used receptor modeling to determine the steelworks contribution to ambient $PM_{2.5}$ concentrations, and found that K, Cl, Cd, and Pb were good tracers for emissions from sintering whereas Mn, F, Zn, and Fe were representative of smelting processes. Mazzei et al. (2006) used principal component analysis (PCA) with varimax rotation to identify particulate matter sources of PM_{10} near a large steel plant located in the harbor area in Genoa (Italy).

Table 2.1. Brief summary of emission sources types, and chemical components in Steel production.

Sector/plant	Plant/operation	Emission type	Components
Ironmaking (230–270º)			
Sinter plant	Iron ore sintering	Point source—continuous	KCl, Fe, Pb, Zn, Mn
	Sinter plant de-dusting	Point source—continuous	Fe, Mn
Blast furnace	Tapping	Fugitive—intermittent	Fe, Mn
	Slag processing	Point source—intermittent	Ca, Al, Si, S
	Stove heating	Stationary source—continuous	CO_2, SO_2, NO_X
Raw materials	Unloading, stocking, blending wind entrainment	Fugitive—intermittent	Fe, Ca, Mg, Mn
Steelmaking/coke making (190–230º)			
BOS plant	Steelmaking	Point source—batch	Fe, Zn, Pb, Mn
	Charging, blowing, tapping	Fugitive—intermittent	Fe, Zn, Pb, Mn
Coke making	Battery underfiring	Point source—continuous	CO_2, SO_2, NO_X, soot (C)
	Charging	Fugitive—intermittent	Organics, particulates
	Door and top leakages	Fugitive—intermittent	Organics, particulates
	Pushing	Fugitive—intermittent	Particulates
	Quenching	Fugitive—intermittent	Particulates, soluble salts
Mills (160–190º)			
Rolling mills	Hot mill	Fugitive—intermittent	Fe, coolants
	Cold mill	Fugitive—intermittent	Lubricants, coolants

However, there is still limited data characterizing the emission of fine and ultrafine particulate matter by iron and steelmaking processes. In the present scenario, there is a need to explore the effect of steel making process on the ambient urban air quality. Thus, a case study was conducted in an Indian steel city, Rourkela, Odisha, to identify the contribution of an integrated steel plant to its urban air pollution.

2.5 AIR QUALITY FORECAST

Air quality modeling plays an important role in formulating air pollution control and management strategies by providing guidelines for efficient air quality planning. Its main

objective is to predict ambient air pollutant concentrations of one and more species in space and time as related to independent variables such as emission and meteorological parameters.

Mathematical tools can provide simulation capabilities, thus offering decision makers with the opportunity to take preventive measures. Two types of mathemetical approaches can be pragmatic for air pollution forecasting, namely (a) using three-dimensional air pollution models which gauge the air pollution levels on a grid basis concerning an area of interest, and (b) using mathematical methods which directly deal the ambient concentrations given in a time series by monitoring stations. In directly dealing with ambient concentrations, several models have been built for predicting air quality. For example, Conventional statistical regression models (Gallero et al. 2006; Guldmann and Kim 2010; Zhao et al. 2010), and time-series analysis (Kumar and Goyal 2011; Mishra and Goyal 2015) were applied. The diversity of forecasting methods that are available does not always ensure full forecasting. It depends on the characteristics of area of interest and the complicated relationships between air quality, meteorology and the effectiveness of the methods used.

In USA, EPA recommended dispersion model, e.g. AERMOD (steady state dispersion model, an advanced version of ISC3) is used for regulatory purposes (Cimorelli et al. 2005). Another EPA recommended model, CALPUFF, is used for long–range transport (source–receptor distances upto 50 km to several hundred km.) of emissions from point, volume, area and line sources (Scire et al. 2000). CALINE 4 is used for highway sources in both urban and rural areas (Benson 1984). In UK, ADMS–urban is used to assess the ambient air quality (Carruthers et al. 2000). In addition, CMAQ (Byun and Schere 2006) is used to assess the ambient air quality (Williams et al. 2011). In developing countries, the availability of precise input data is one of the challenges. In spite of this, AirQuis modeling system has been developed in South Africa, which is being used for UAQMP in the city of eThekwini (NIUL 2007). Besides, in the designated air shed priority areas, CALPUFF is used to forecast

the ambient air quality as a part of UAQMP (DEAT 2008). At a local scale, Zunckel, (2009) has developed an air pollution information network, which comprises guidelines/recommendations on how to carry out efficient air quality modeling. However, in Mexico City, coupled WRF–Chem (a photo chemical model) is mainly used to forecast the pollutant concentrations (Li et al. 2011; Tie et al. 2007; Ying et al. 2009). In India, Gaussian based dispersion air quality models are used for regulatory compliances of ambient air quality (CPCB 2010). In addition, a number of air quality models/codes have been validated/developed to predict ambient air quality in selected air quality control regions (Gokhale and Khare 2005; Kesarkar et al. 2007; Khare and Sharma 1999; Luhar and Patil 1989; Sharma et al. 2013). In addition, Elbir, (2004); Elbir et al., (2010); Gulliver and Briggs, (2011); Schipa et al., (2011) have used geographical information system (GIS) coupled with air quality models to forecast the pollutant concentrations in ambient urban environments.

Recent studies have embraced artificial neural network (ANN) models as an alternative to traditional statistical forecasting methods such as linear regression techniques (Cortina-Januchs et al. 2015). Given the success of ANNs in forecasting and the urgent need for robust forecasts, the present research explores the efficacy of ANN approaches in forecasting particulate matter (PM) concentrations using meteorological data as inputs. In particular, it tries to compare the performances of multilayer perceptron (MLP) and radial basis function (RBF) algorithms in forecasting. In so doing, the aim is not to refine predictive models for operational use but to provide a rigorous inter-comparison as a first step toward operational PM forecasting models.

2.6 GAPS IN KNOWLEDGE

The gaps in the knowledge prior to the design and implementation of present research work identified during the course of literature review are as follows:

- Very few studies on seasonal variations of PM and their causes in India.
- Very few studies on identification and apportionment of particulate pollution sources based on ambient air concentrations in urban regions of India.
- Minimal evaluation of ambient air pollutants in steel cities worldwide and almost negligible in India.
- Limited studies on receptor model applications like CMB, PCA, PMF and their comparison in India.
- Very few discussions on forecasting methodologies for ambient air pollution in Indian cities.
- Very few studies giving stress on working hours of a day where the exposure to the ambient air pollution is much higher.

The present research work has been designed to address the gaps in knowledge listed above and to provide a noteworthy support to the literature by achieving research objectives as described below.

2.7 RESEARCH OBJECTIVES

- To chemically characterize and analyze seasonal variations of ambient PM.
- To develop the source profiles for road dust and soil dust in Rourkela.
- Identification and apportionment of air pollutants in Rourkela using Chemical Mass Balance model, Principal Component Analysis and Positive Matrix Factorization.
- Development of a semi-empirical model to predict pollutant concentration in any of the steel city from data on characterization and location of the different units as well as geographical and meteorological data.

CHAPTER3- PM SAMPLING AND CHEMICAL ANALYSIS

3 PM SAMPLING AND CHEMICAL ANALYSIS

Air pollution monitoring and analysis involves huge resources because of the high variability in air quality parameters. The designing of a monitoring programme requires the following steps to be considered:

- Selection of sites
- Monitoring parameters
- Monitoring instrumentation and method selection
- Quality assurance
- Sample analysis

3.1 SITE SELECTION CRITERIA

Selection of representative site for monitoring is the crucial step in approaching the objectives of the study. Monitoring site should not be influenced by any direct source of the pollutant. The common criteria used in the selection of air quality monitoring sites is that each sampling location measures an air mass that is representative of relatively large land area (Noll and Miller 1977). Following considerations were also given weightage while selecting the sites for the present study.

a) Realistic representation of receptors and emission sources under study.

b) Area wise representation.

c) No nearby major obstruction to wind flow.

d) Uniformity in height above the ground level is desirable for the entire network within the region.

e) The following factors were also considered for the siting of a station.

- An elevation of 0.9–1.8 m is suggested as the most suitable for representative sampling, especially in residential sites.
- An obstacle should not intersect a 45º cone inscribed on the vertical axis of the sampling instrument.
- The surrounding area should be free from stacks, chimneys or other local emission points.
- Sampler should be 30 cm from any obstacle to air flow and at a distance 5–20 m from roadways.

f) Practical considerations such as :

- Availability of electric power.
- Site accessibility.

Some of the principal factors governing the locations of the monitoring sites are the objectives, method of instrument used for sampling, available resources, physical access, feasibility and security against loss and tampering. Considering the objectives of the study, the network of an ideal system of location of sampling sites is in the form of a grid, which may be rectangular or radial depending upon the sources of pollution.

The monitoring site where the sampling instrument is located should also fulfill one or more of the following requirements depending on the types of instruments used:

- it should be available for an extended period of time;
- it should preferably be accessible any time throughout the year;

- electrical power of sufficient rating should be available;
- it should be vandal-proof, and
- It may need to be protected from extreme of temperatures and other climatic conditions.

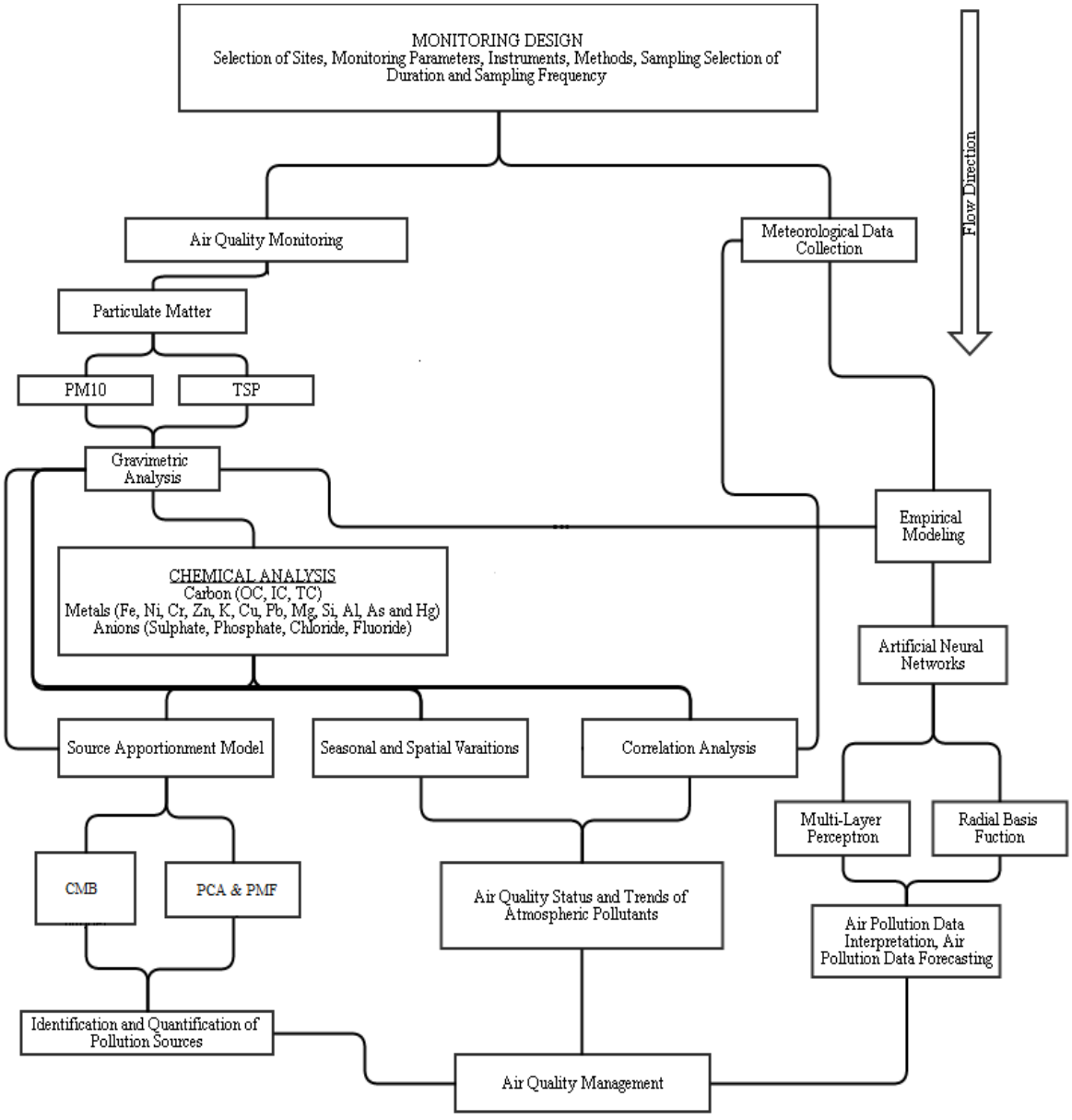


Figure 3.1. Detailed study program.

3.2 STUDY AREA

Steel city, Rourkela (22°12' N, 84°54' E) with a mean sea level of about 219 m is selected as a study area in the present research work. It is one of the most important industrial cities in Sundargarh district of Odisha, India. It is located at the heart of a rich mineral belt and surrounded by a range of hills and encircled by rivers. As per 2011 census report of India, population of Rourkela is about 689,298 and is growing rapidly. The city is spread over an area of 121.7 km^2 in close proximity of iron ore, dolomite, limestone and coal belts. The perennial Koel River flows through this valley and meets another perennial river Sankh at Vedavyas, on the outskirts of Rourkela. It has a tropical climate having average annual rainfall between 160 cm and 200 cm.

Four monitoring sites have been selected for the present ambient air quality study as shown in figure 3.2. The monitoring sites have been chosen based on the anthropogenic activities. The sampling duration and sampling frequency has been decided based on the local anthropogenic activities and monitoring feasibility. Table 3.1 summarizes the details of sampling sites. Figure 3.3 shows seasonal wind rose plot for Rourkela city during the sampling period. The wind direction has been observed predominantly in southwest direction throughout the year.

There may be certain differences in ambient air from locality to locality such as from a commercial area to a residential area. To negotiate these differences and to get an overall view of ambient air quality, four monitoring sites have been selected for the present ambient study. The first site is Indira Gandhi Park which is a calm residential area and the second site is Udit Nagar which is a commercial residential area with a lot of commercial activities such as markets and shopping complexes. The third monitoring site is IDL Colony that is surrounded by different industries and is adjacent to national highway. The fourth monitoring site is National Institute of Technology (NIT) campus which is a residential locality. In the

present research work, the air pollution sources that have been considered are located in a surrounding area of 10 km x10 km grid around monitoring sites for identification of possible air pollution sources.

Table 3.1. Details of sampling sites in Rourkela city.

S. No.	Sampling Site	Description	Dominant Anthropogenic Activity
1	Indira Gandhi Park	Residential	Residential with moderate vehicular traffic
2	Udit Nagar	Commercial	Residential with heavy vehicular traffic and commercial complexes
3	IDL Colony	Industrial	Industrial, rural area, adjuscent to national highway and heavy vehicle traffic
4	NIT main building rooftop	Residential	Educational and residential campus having nearby rural areas with very low vehicular traffic

Figure 3.2. Monitoring sites present in the study area.

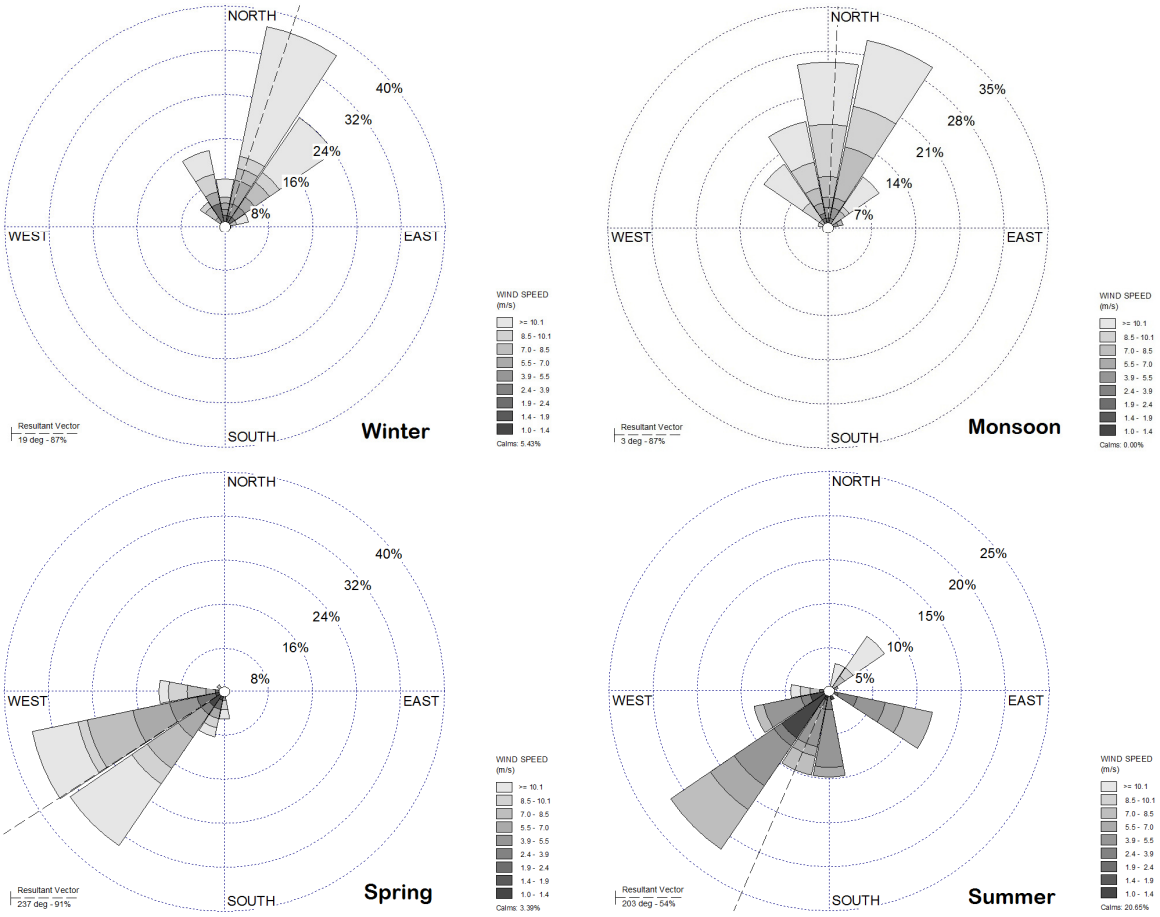


Figure 3.3. Seasonal Windrose diagram of Rourkela City during the sampling period.

3.3 MONITORING PROTOCOL

3.3.1 SAMPLING AND ANALYZING INSTRUMENTS

Several instruments were used for air quality sampling and chemical analysis purposes in the present study. The details of different instruments used and their purpose are summarized in table 3.2.

3.3.2 AIR SAMPLING

The air quality sampling setup has been designed according to the Indian Standard IS 5182 (Part 23): 2006(IS5182 2006). Figure 3.4 shows the sampling setup (NETEL, NPM-HVS/R) for PM_{10} and TSP sampling. The instrument when switched on, it separates particles with

aerodynamic diameters below 10μm using cyclonic flow technique having a pump to draw air at a rate of 1000 lpm. The separated particles were then collected onto a glass fiber microfiber filter paper (size 20.3X25.4 cm).

Table 3.2. Different instruments used on the present project and their applications.

S.No	Instrument	Make	Usage
1	Respirable Dust Sampler	NETEL, NPM-HVS/R	Monitoring of PM_{10}, TSP
2	Muffle Furnace	REICO	Baking of filter papers
3	Desiccator	Borosil	Equilibration of filter papers
4	Balance	Sartorius CPA 124S	Weighing of filter papers and chemicals
5	Fume Hood	REICO	Acid digestion of filter papers, dust and soil samples
6	Ultra-Sonication Bath	Labman LMUC-2	Extraction of water soluble ions
7	UV-Visible Spectrophotometer	Perkin Elmer Lambda 35	Quantitative determination of different analytes
8	Atomic Absorption Spectrophotometer	Perkin Elmer AAnalyst 200	Analysis of cations and elements
9	Total organic carbon analyzer	Shimadzu TOC-V CPH/CPN	Analysis of TOC, IC and TC
10	Fluoride Electrodes	Thermo Scientific Orion 9409BN Half-Cell Fluoride and Orion 9609BNWP Combination	Analysis of F^-

The filter papers were calcined at 400 °C for 2 h to remove any organic compounds that may be present on filters (Kong et al. 2010) and then equilibrated in a desiccator before sampling (Karar et al. 2006; Karar and Gupta 2006).

The amount of air sampled through the weighted filter paper is recorded and the filters are placed in appropriately labeled envelopes and transported along with blank filter to the laboratory for analysis. Field and laboratory blank filter samples were routinely analyzed to evaluate analytical bias and precision. Sampling was carried out in spring, summer, autumn and winter of 2011 and 2012. Sampling duration of each sample is 8 h from 9:00 AM to 5:00 PM and a total of 196 samples were collected. Prior to measurement, the flow rate of the sampler was calibrated. Sampling has been done twice in a week, preferably one on a weekday and another on a weekend during the study period of two years.

3.3.3 ROAD DUST AND SOIL DUST SAMPLING

Paved road dust samples were collected by sweeping an area of 1m x10 m from middle of the road surface for development of its source profile. The dust present on road surface in the selected area was collected by using a paint brush of 5-inch width. All the dust samples were swept towards the middle of selected area and then collected into the sampling bags and brought to the laboratory.

Soil samples were collected by sweeping the soil surface of an area of 1m x10m for development of soil dust source profile. The selected soil surface is about 10 m away from the road. The soil dust samples were collected by using a paint brush of 5-inch width and brought to the laboratory for its further chemical characterization.

Total of 114 road dust samples and 114 soil dust samples were collected during the study period. Once the road dust and soil dust samples were brought to the laboratory, these samples were spread in petri dishes and kept in hot air oven at temperature of 120 °C for 24 h to remove moisture content of the samples. After drying, paved road dust and soil dust

samples were equilibrated to room temperature in a desiccator. The dust samples were then sieved by using a mesh of 90µm pore size. Thus, the fraction of 0-90 µm particle size was separated for source profiling purpose. The chemical analysis of these samples had been performed in the same manner as that of PM_{10} and TSP samples. There is a possibility that even at that size, heavier particle may not suspend in air. There is another possibility that lighter particles bigger that that size may suspend in air due to low density. This limitation in directly analyzing raw samples when compared to resuspension chambers.

Figure 3.4. NETEL, NPM-HVS/R Respirable Dust Sampler.

3.3.4 CHEMICAL ANALYSIS OF PM

The PM_{10} concentrations were measured gravimetrically by weighing the particulate mass deposited on the quartz microfiber filters and knowing the total volume of air sampled. All the filter papers were weighed by a sensitive microbalance (Sartorius CPA 124S) with balance sensitivity of ±0.1mg. Prior to weighing, the filters were equilibrated in a desiccator at room temperature for 48 h (Karar et al. 2006; Karar and Gupta 2006; Kong et al. 2010).

3.3.4.1 EXTRACTION OF TRACE METALS

After gravimetric analysis, a fraction of the exposed filter papers was digested in HNO_3 (nitric acid) and used for trace metal analysis (APHA and AWWA 2012). For trace metal analysis, 40 punch holes (each of 0.20 cm^2) of the exposed fiber filters with an area of 8 cm^2 were acid digested. After digestion, a colorless solution so obtained was evaporated to dryness. Reagent blank had also been prepared by using conditioned unexposed filter paper following the similar procedure. Cool filtrate was made to a known volume using freshly prepared distilled water and is analyzed for metal constituents using Atomic Absorption Spectrophotometer (AAnalist200, Perkin Elmer) (Figure 5) for iron (Fe), nickel (Ni), chromium (Cr), zinc (Zn), potassium (K), copper (Cu), lead (Pb), magnesium (Mg), silicon (Si), aluminium (Al), arsenic (As) and mercury (Hg). During sample analysis, standard solution was repeatedly aspirated to ensure that the calibration was within the limits of control chart.

Figure 3.5. Perkin Elmer AAnalyzer 200 atomic absorption spectrophotometer.

3.3.4.2 EXTRACTION OF IONS

For determination of water soluble ionic species, 40 punch holes (each of 0.20 cm^2) of the exposed fiber filter papers with an area of 8 cm^2 were sonicated three times in 20 ml of double distilled water for 30 min in an ultrasonic bath (Labman LMUC-2). An intensive quality control program was implemented to maintain the accuracy and precision throughout the study. The concentration of F^- was measured by using The Thermo Scientific Orion 9409BN Half-Cell Fluoride and Orion 9609BNWP Combination Fluoride Electrodes. Whereas the concentration of SO_4^{2-} was determined according to Indian standard IS 3025(Part 24): 1986 by adding barium chloride to the solution upon which it gives a thick white precipitate of barium sulphate which can be measured by spectrophotometrically (Figure 3.6). The concentration of Cl^- was determined according to the Indian standard IS 3025(Part 32): 1988 by using Argentometric method. The concentration of phosphate was determined according to Indian standard IS 3025(Part 31):1988.

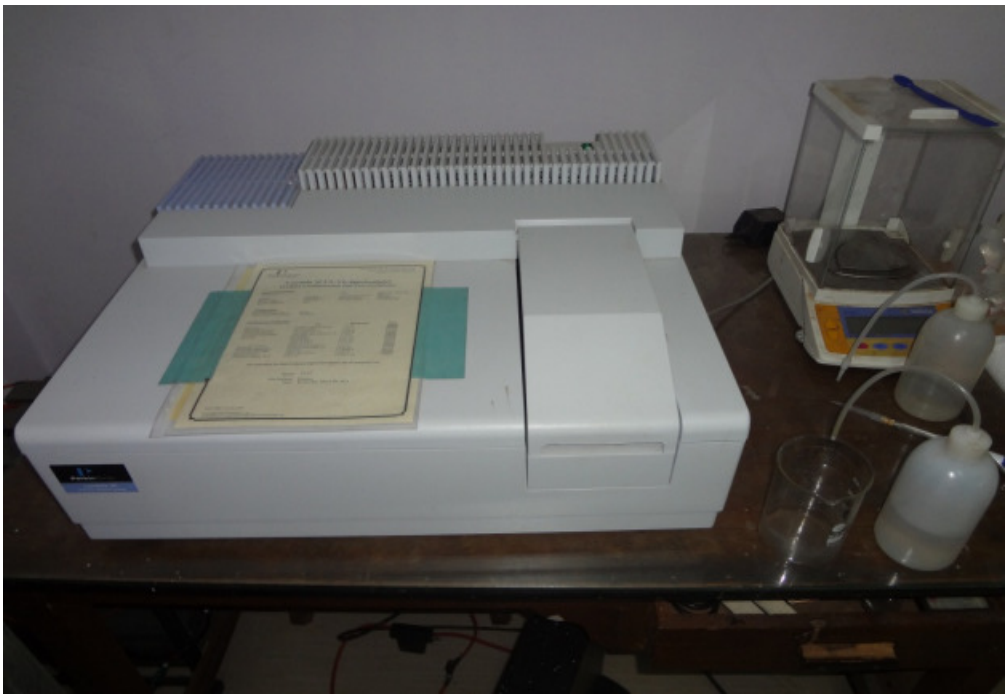


Figure 3.6. Perkin Elmer Lambda 35 UV-Visible Spectrophotometer.

3.3.4.3 Analysis of Carbon Species

The total carbon (TC) and total organic carbon (TOC) contents of PM_{10} and TSP samples have been determined by using a SHIMADZU TOC-V CPH/CPN Analyzer (Figure 7).

Figure 3.7. Shimadzu TOC-V CPH/CPN total organic carbon analyzer.

3.4 QUALITY ASSURANCE AND QUALITY CONTROL

Data quality must be assured through the application of quality control and quality assurance procedures. Quality control is the system of activities to provide a quality product, whereas quality assurance is meant to protect against failures in quality control. Quality control usually includes checks performed during normal internal procedures. Quality assurance refers to more occasional activities, such as on-site system surveys and periodic evaluation of internal quality control data. The most critical requirement is the availability of adequately trained and properly motivated personnel and appropriate facilities for the execution of defined tasks in the monitoring program. Secondly, the design of sample collection should be as such the collection of representative samples is ensured. Thirdly, instrumental analysis should follow techniques validated with relevant reference materials whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed. Next, is the quantification stage, in which, concentrations of analytes in the sample are calculated using calibration curve derived from authentic standards.

The present study ensured the following quality assurance and control procedures:

[1] Maintenance and service was done at frequent periods of the equipment used for monitoring and analysis procedures.

[2] Collection of representative samples with proper labeling (sample type, location, time and date of collection, environmental characteristics, etc.) was ensured.

[3] The expendable material, e.g., glassware, solvents, etc. were used with suitable quality.

[4] Concentrations of analytes in the sample were calculated using calibration curve derived from authentic standards.

[5] Acceptance tests for the instruments and apparatus being used.

[6] Quality control during field operation and chemical reagent handling.

[7] The flow rate of the pump was calibrated using a rotameter and monitored at an interval of 1 h.

[8] Routine calibration to ensure that the flow rates were maintained in an acceptable range.

[9] Filter handling was cautious, using clean forceps.

[10] Ultimate care was taken during the sampling, sample handling, processing and analysis to avoid any contamination.

[11] Data quality control by means of collocated sampling, flow audit, spot check and duplicate analysis.

[12] Competence tests of field operators and laboratory analysts.

In this study, each filter paper was weighed 3 times before and after sampling and the average value has been considered for calculation. The filters were folded, packed and preserved in envelopes with proper labeling when they were not used. All the glassware was acid washed and oven dried to avoid any sort of contamination among samples. For checking accuracy of elemental analysis, known standard solution was prepared by diluting of Merck standard solution for AAS.

The values of the known solution lie within 95 % of certified values. Background contamination was routinely monitored by using operational blanks which were processed simultaneously with field samples. As per USEPA protocol, 7 number of laboratory blanks and 7 number of field blanks collected as part of QA/QC. The determination of concentrations of chemical components in blank filter papers was performed by the similar process as that of monitored samples. Those values were subtracted from the sample values to correct the final data. Limit of Detection (LOD), and Limit of Quantitation (LOQ) are terms used to describe the smallest concentration of a measurand that can be reliably

measured by an analytical procedure. The limit of detection (LOD) was estimated as the concentration corresponding to three times the standard deviation of the blank values (3σ) obtained from the set of reagent blanks. Similarly, limit of quantification (LOQ) was estimated as 10 times the standard deviation of the blank values (10σ) (MacDougall and Crummett 1980). The LOD and LOQ values of different chemical constituents were presented in table 3.3.

Table 3.3. Limit of detection (LOD) and Limit of quantitation (LOQ) for different chemical constituents of TSP.

Chemical constituent	**LOD (ng/m^3)**	**LOQ (ng/m^3)**
Fe	33.82	112.74
Ni	1.24	4.14
Cr	1.59	5.29
Zn	6.40	21.32
K	12.44	41.46
Cu	2.11	7.02
Pb	1.38	4.59
Mg	4.02	13.39
Si	5.29	17.63
Al	3.56	11.86
As	0.24	0.80
Hg	0.09	0.29
Cl^-	7.31	24.37
PO_4^{2-}	0.50	1.68
F^-	0.32	1.08
SO_4^{2-}	7.67	25.57
TOC	26.12	87.06
IC	9.43	31.42
TC	23.39	77.96

CHAPTER 4- CHEMICAL CHARACTERIZATION AND DATA ANALYSIS

4 CHEMICAL CHARACTERIZATION AND DATA ANALYSIS

Particulate pollution in an urban atmosphere is an intricate phenomenon as it consists of different types of chemical species originated from different types of activities. To understand the effect of particulate pollution on human beings and ecosystem, a detailed chemical characterization of particulate matter (PM) is required. In doing so, not only the chemical constituents are quantified but also a comprehensive data analysis is conducted. The data analysis helps in discovering the trends and patterns present in chemical composition of PM. This in turn helps in understanding the parameters that influence the organization and distribution of PM in atmosphere. Data analysis includes seasonal, correlations among the chemical species and enrichment factor analysis which gives a basic idea about the crustal origins of PM. The present chapter concentrates on presenting the detailed chemical characterization and data analysis of PM_{10} and TSP for urban region of an Indian steel city, Rourkela. Thus the main components of chapters include:

- Chemical constituents
- Seasonal Variation
- Correlation analysis
- Enrichment factor analysis

4.1 CHEMICAL CONSTITUENTS

The 8h (9am to 5pm) average values of PM_{10} obtained during January 2011 to December 2012 are in the range of 80.88 μg/m^3 to 225.93 μg/m^3 whereas, that of TSP ranged from 88.93 to 262.04 μg/m^3. The wide range of mass concentration is due to extreme weather conditions like temperature (6°C-47°C), relative humidity (40-97) and heavy rain falls during monsoon (up to 8 cm/d). Significant amount of metals like Fe, Zn, K, Mg and Al were observed both in PM_{10} and TSP during study period (Table 4.1). Apparently higher iron concentration in aerosol may be due to influence of nearby iron and steel industry and also of its abundance in crustal sources. The chemical characterization of PM_{10} mass showed an abundance (up to 55%) of crustal elements (Al, Fe, Mg and K) followed by 35% of carbon compounds (TOC, IC, TC), 8% of anions (Cl^-, SO_4^{2-}, F^- and PO_4^{3-}) and 2% of other trace elements (Zn, Cr, Cu, Ni, Pb, Hg and As). Whereas the chemical characterization of TSP revealed that up to 56% of constituents were crustal elements (Al, Fe, Mg, Si and K), 34% were carbon compounds (TOC, IC and TC), 8% were anions (Cl^-, SO_4^{2-}, F^- and PO_4^{3-}), and 2% were trace elements (Zn, Cr, Cu, Ni, Pb, Hg and As).

Ambient aerosol consist mostly oxides of aluminum, silicon, calcium, zinc, iron and other metals (Chow and Watson 1992). The precise combination of these minerals depends on geology of the area and industrial processes. According to geology of Rourkela city, it is surrounded by iron ore mines along with industries like steel-making, smelting, mining and cement production. Hence the concentration of iron is predominant among the metals. The major sources of Fe are both anthropogenic and crustal origin, they include iron and steel manufacturing units and weathering of exposed iron in urban areas (Lee et al. 1994).

Chronic exposure to Fe may cause benign Pneumonia-conuisis and can enhance harmful effects of SO_2^{4-} and various carcinogens. Ingestion of Fe in excessive quantity inhibits the activity of many vital enzymes (Khillare et al. 2004). Abundance of Al and Si in

PM in Rourkela are mostly due to iron ore mining and processing of ore. Presence of Zn and Cu in aerosol indicates frequent application of brakes and confirms the contribution of vehicular emissions at the study site (Srimuruganandam and Shiva Nagendra 2012).

Table 4.1. Mass concentration of different chemical species present in PM_{10} and TSP during the study period.

Species	Unit	PM_{10}	TSP
Fe	ng/m^3	9035.52±2565.96	10137.34±2921.99
Ni	ng/m^3	15.70±4.47	17.38±4.97
Cr	ng/m^3	27.99±7.99	30.82±8.75
Zn	ng/m^3	228.60±60.45	252.06±62.02
K	ng/m^3	3341.74±870.13	3635.42±940.85
Cu	ng/m^3	7.26±3.84	16.77±20.15
Pb	ng/m^3	13.87±5.21	17.14±6.44
Mg	ng/m^3	279.24±78.30	608.63±221.29
Si	ng/m^3	105.76±43.32	128.02±48.65
Al	ng/m^3	488.64±130.45	546.42±149.95
As	ng/m^3	0.54±0.69	0.85±1.06
Hg	ng/m^3	0.18±0.26	0.18±0.26
Cl^-	ng/m^3	249.96±66.00	251.04±66.12
PO_4^{3-}	ng/m^3	2.39±0.76	3.79±1.39
F^-	ng/m^3	1.50±0.46	1.72±0.55
SO_4^{2-}	ng/m^3	1630.83±467.33	1872.06±559.26
TOC	ng/m^3	4057.32±1095.46	7902.86±2120.27
IC	ng/m^3	11.65±4.84	272.65±102.77
TC	ng/m^3	4068.98±1098.47	8175.51±2200.83

Also Zn and Pb are trace elements emitted from fossil fuels. Until a decade ago (Rastogi and Sarin 2009), one of the major sources of atmospheric Pb was vehicular emission but the ban on leaded petrol (in 2007) decreases its atmospheric abundance. Other important sources of Pb in Rourkela are the battery industry, backyard smelting as well as refuse burning other than automobiles.

Since the major sources of sulfate are fossil fuel burning and industrial activities, comparatively higher mass fraction of SO_4^{2-} indicates the anthropogenic influence in study area. Sulfate particles are an important component of the aerosol in urban areas of Rourkela mainly originating from gas to particulate conversion. Mass concentration of fluoride in air could be due to crustal origin or from nearby industrial sources like fertilizer plants and coal operations. The e-waste has also its influence on occurrence of Cu, Pb, Al, Hg and As in TSP aerosol.

4.2 SEASONAL VARIATIONS

The large diversity in aerosol sources can cause significant variation in their chemical composition. To study the seasonal variation of aerosol mass, the observed data for the entire period are grouped according to the different seasons. The climate of Rourkela reflects its summer of the year from April to June which is associated with strong winds, low humidity that can substantially increase the level of ambient particulates. In contrast, the monsoon of the year from July to September is associated with low wind speeds and medium to heavy precipitation, reduces the air pollution potential of Rourkela. The winter from October to December and spring from January to March of the year is associated with low wind speeds and negligible rainfall resulting in increase of the air pollution level of Rourkela. Seasonal variations of PM_{10} and TSP are summarized in tables 4.2 and 4.3 respectively. From tables it

can be observed that during spring and summer, particulate matter was generally high in concentration whereas during monsoon it is low.

Figures 4.1 and 4.2 represent the seasonal variations of chemical constituents of PM_{10} and TSP respectively. From the figures it was observed that almost all the constituents of PM_{10} and TSP have followed same trend according to seasons i.e. summer> spring> winter> monsoon.

Mineral dust is one of the contributors of the aerosol composition during all seasons. From the two years measured aerosol data at urban region of Rourkela, it can be predicted that monsoon does affect the atmospheric turbidity with a decrease in aerosol concentration due to wet scavenging and increase in mostly post-monsoon period. Precipitation in monsoon results in washout of PM making atmosphere comparatively clean from dust particles. During rainy season, particulate matter concentration diminished, while reduction in metal concentration is very transparent. In case of copper, its concentration during monsoon is higher than that of winter. This suggests that copper is not precipitated and washed by rain in a big proportion because it may be present in finer fraction of respirable size and stay in the atmosphere in spite of pluvial precipitation.

Table 4.2. Seasonal Statistics of PM_{10} and its elemental and ionic constituents during the study period at Rourkela.

		PM_{10}	Fe	Ni	Cr	Zn	K	Cu	Pb	Mg	Si	Al	As	Hg	Cl^-	$PO4^{2-}$	F^-	SO_4^{2-}	TOC	IC	TC
Spring (n=33)	**Minimum**	89.91	6206.74	10.86	19.34	144.79	2237.07	1.28	7.55	190.54	59.29	329.99	0.00	0.00	113.47	1.23	0.96	1120.25	3012.55	5.65	3021.49
	Maximum	200.88	14987.15	26.10	46.05	349.47	4883.37	17.58	33.44	452.67	257.77	808.52	2.41	1.06	475.53	4.07	3.03	2684.04	6464.95	26.40	6484.15
	Mean	150.89	10550.10	18.46	32.79	262.23	3783.49	8.67	16.86	325.99	139.77	567.84	0.70	0.15	259.42	2.45	1.88	1911.87	4875.46	12.89	4888.35
	Median	152.98	10473.41	18.91	33.21	269.76	3967.00	7.86	16.46	326.30	135.95	579.14	0.50	0.05	246.43	2.37	1.88	1917.73	4790.04	12.65	4804.26
	SD	33.10	2381.78	4.18	7.42	57.33	778.28	4.30	6.03	72.71	49.64	116.68	0.67	0.27	90.02	0.70	0.53	438.42	978.43	4.85	980.45
Summer (n=41)	**Minimum**	89.12	7481.97	13.02	23.18	173.79	2751.14	0.97	2.94	227.14	38.92	370.58	0.00	0.00	123.27	1.23	1.23	1350.59	3156.87	3.33	3160.20
	Maximum	225.93	17717.48	31.03	55.16	438.31	6196.28	13.27	26.47	541.73	198.03	903.86	3.13	0.64	398.02	4.09	2.77	3209.61	7715.53	37.61	7753.14
	Mean	149.09	11625.03	20.15	36.00	287.79	4211.13	5.07	15.50	358.35	111.99	615.71	0.58	0.12	261.39	2.56	1.87	2098.98	4987.79	14.64	5002.43
	Median	146.76	11318.20	20.14	34.85	274.35	4020.93	4.56	16.10	353.40	111.24	578.72	0.22	0.05	260.79	2.42	1.82	2029.88	4834.89	14.26	4853.89
	SD	36.88	2896.28	5.07	9.00	67.99	964.37	3.33	5.40	88.21	37.25	150.97	0.88	0.15	62.73	0.81	0.45	526.17	1239.23	6.71	1244.16
Monsoon (n=50)	**Minimum**	80.88	5578.46	9.59	17.09	147.70	1949.09	0.66	2.58	167.90	22.29	306.39	0.00	0.00	140.48	1.23	0.89	995.52	2575.71	3.51	2582.56
	Maximum	160.29	12805.58	21.37	39.24	309.55	4372.32	13.06	21.56	391.23	184.57	635.80	2.06	1.09	393.14	4.48	1.69	2283.44	5443.61	15.80	5453.02
	Mean	105.86	7619.00	13.22	23.58	197.26	2918.65	7.28	12.53	236.18	91.92	422.30	0.40	0.24	245.55	2.32	1.24	1373.70	3395.80	9.53	3405.33
	Median	107.39	7576.62	13.12	23.46	199.49	2940.33	7.75	12.80	236.62	86.45	423.16	0.16	0.07	247.08	1.96	1.23	1363.48	3446.98	9.82	3456.76
	SD	14.24	1160.38	1.95	3.57	29.77	465.13	3.39	4.41	35.25	33.27	59.83	0.51	0.33	57.37	0.86	0.22	207.51	467.86	2.58	468.41
Winter (n=72)	**Minimum**	81.12	5697.17	9.90	17.63	140.22	1827.12	0.77	2.96	182.04	13.96	313.13	0.00	0.00	85.68	1.31	0.77	1027.13	2619.92	3.96	2631.64
	Maximum	190.30	13007.79	23.45	40.78	316.90	5102.76	16.20	25.36	404.58	213.03	704.34	3.13	1.06	365.45	3.92	2.33	2419.05	6052.76	24.35	6070.73
	Mean	112.63	7850.45	13.64	24.29	201.26	2938.02	7.84	12.50	242.65	96.23	426.05	0.54	0.17	242.18	2.31	1.30	1414.00	3611.89	10.86	3622.75
	Median	106.83	7504.11	13.23	23.32	195.40	2971.96	7.04	12.47	232.48	96.16	407.89	0.23	0.05	234.00	2.27	1.32	1359.42	3432.38	10.59	3444.88
	SD	22.55	1447.62	2.51	4.54	36.62	560.94	3.74	4.42	43.85	41.36	77.31	0.68	0.24	60.26	0.66	0.29	264.58	694.76	3.57	696.21

Units for PM_{10} are in $\mu g/m_3$ and units for chemical species are in ng/m_3

Table 4.3. Seasonal Statistics of TSP and its elemental and ionic constituents during the study period at Rourkela.

		TSP	Fe	Ni	Cr	Zn	K	Cu	Pb	Mg	Si	Al	As	Hg	Cl^-	PO_4^{2-}	F^-	SO_4^{2-}	TOC	IC	TC
Spring (n=33)	**Minimum**	103.42	7833.51	13.21	22.94	184.48	2672.81	2.59	12.63	535.94	92.21	410.86	0.00	0.00	113.47	1.47	1.04	1429.98	5772.85	110.68	6070.48
	Maximum	221.93	16802.93	28.56	50.49	403.59	5462.00	98.73	33.97	1436.23	264.95	900.60	2.99	1.06	479.22	6.79	3.08	3148.90	12583.42	536.42	13119.84
	Mean	167.68	12323.60	21.14	37.39	304.15	4258.48	19.88	20.76	853.72	167.31	659.56	1.13	0.15	260.54	3.88	2.17	2287.34	9497.25	331.52	9828.77
	Median	164.43	11631.31	19.82	34.93	303.24	4314.78	13.54	20.74	838.90	164.38	620.92	0.83	0.05	246.58	3.75	2.15	2176.99	9359.39	328.87	9652.23
	SD	33.78	2605.68	4.35	7.75	57.01	807.35	19.80	4.82	237.17	44.41	128.91	0.99	0.27	89.40	1.36	0.48	498.43	1915.78	101.01	1982.64
Summer (n=41)	**Minimum**	109.73	8330.71	13.43	24.95	174.01	2993.06	1.45	8.84	464.19	83.16	413.54	0.00	0.00	124.41	1.75	1.24	1529.83	6221.71	120.57	6351.00
	Maximum	262.04	19885.19	35.21	60.87	464.56	6546.30	124.19	42.09	1227.39	297.20	1028.22	6.07	0.64	399.32	7.76	3.70	3749.63	14930.22	539.31	15381.57
	Mean	171.21	12930.68	22.05	39.01	294.67	4523.61	25.68	21.63	746.13	151.89	687.56	0.99	0.12	262.46	4.04	2.21	2422.05	9703.23	342.91	10046.14
	Median	164.83	12360.43	20.83	37.36	285.85	4297.36	10.58	20.22	714.95	142.12	634.08	0.45	0.05	261.07	3.79	2.01	2303.03	9317.06	365.42	9675.72
	SD	40.48	3087.14	5.46	9.49	68.78	1011.56	33.95	8.17	190.31	50.02	162.78	1.47	0.15	62.08	1.50	0.60	581.80	2384.49	110.99	2475.68
Monsoon (n=50)	**Minimum**	89.34	6239.80	10.75	19.16	147.80	2159.08	1.93	3.07	370.86	34.88	340.59	0.00	0.00	140.48	1.23	1.04	1117.83	5066.14	36.47	5254.78
	Maximum	189.44	14328.79	24.38	43.10	320.98	4824.35	72.18	23.48	860.89	190.26	719.57	2.27	1.09	395.94	7.34	2.43	2687.86	10741.04	460.79	11201.83
	Mean	116.71	8434.98	14.47	25.67	215.28	3140.98	13.69	15.19	482.32	109.62	465.02	0.66	0.24	246.65	3.63	1.44	1553.46	6623.93	219.41	6843.34
	Median	118.51	8293.05	14.35	25.58	212.50	3173.55	10.17	16.21	456.18	102.16	469.37	0.48	0.07	247.39	3.49	1.45	1527.71	6719.74	220.52	6956.61
	SD	16.28	1287.42	2.13	3.75	30.59	476.50	12.98	4.92	97.18	34.30	66.21	0.71	0.33	57.07	1.44	0.28	252.97	918.50	66.87	965.42
Winter (n=72)	**Minimum**	88.93	6333.90	11.01	19.61	150.68	2024.99	1.51	4.65	332.40	21.51	343.28	0.00	0.00	87.13	1.31	0.87	1142.53	5042.14	63.80	5146.32
	Maximum	207.78	15673.31	26.11	47.16	354.13	5706.15	66.84	27.48	1169.33	219.01	837.66	5.34	1.06	366.79	6.37	2.33	2891.23	11781.13	415.56	12196.69
	Mean	123.99	8726.83	15.01	26.71	229.47	3187.44	12.40	14.28	505.71	109.20	470.72	0.78	0.17	243.24	3.71	1.44	1589.78	7035.03	242.63	7277.66
	Median	117.78	8385.79	14.44	25.79	219.99	3217.72	11.72	13.98	486.31	110.65	451.15	0.52	0.05	235.22	3.68	1.45	1531.99	6708.28	239.18	6949.96
	SD	23.98	1707.75	2.84	5.18	43.72	610.71	8.78	4.35	142.75	40.94	88.98	0.97	0.24	59.94	1.26	0.28	314.51	1353.58	81.77	1400.93

Units for TSP are in $\mu g/m_3$ and units for chemical species are in ng/m_3

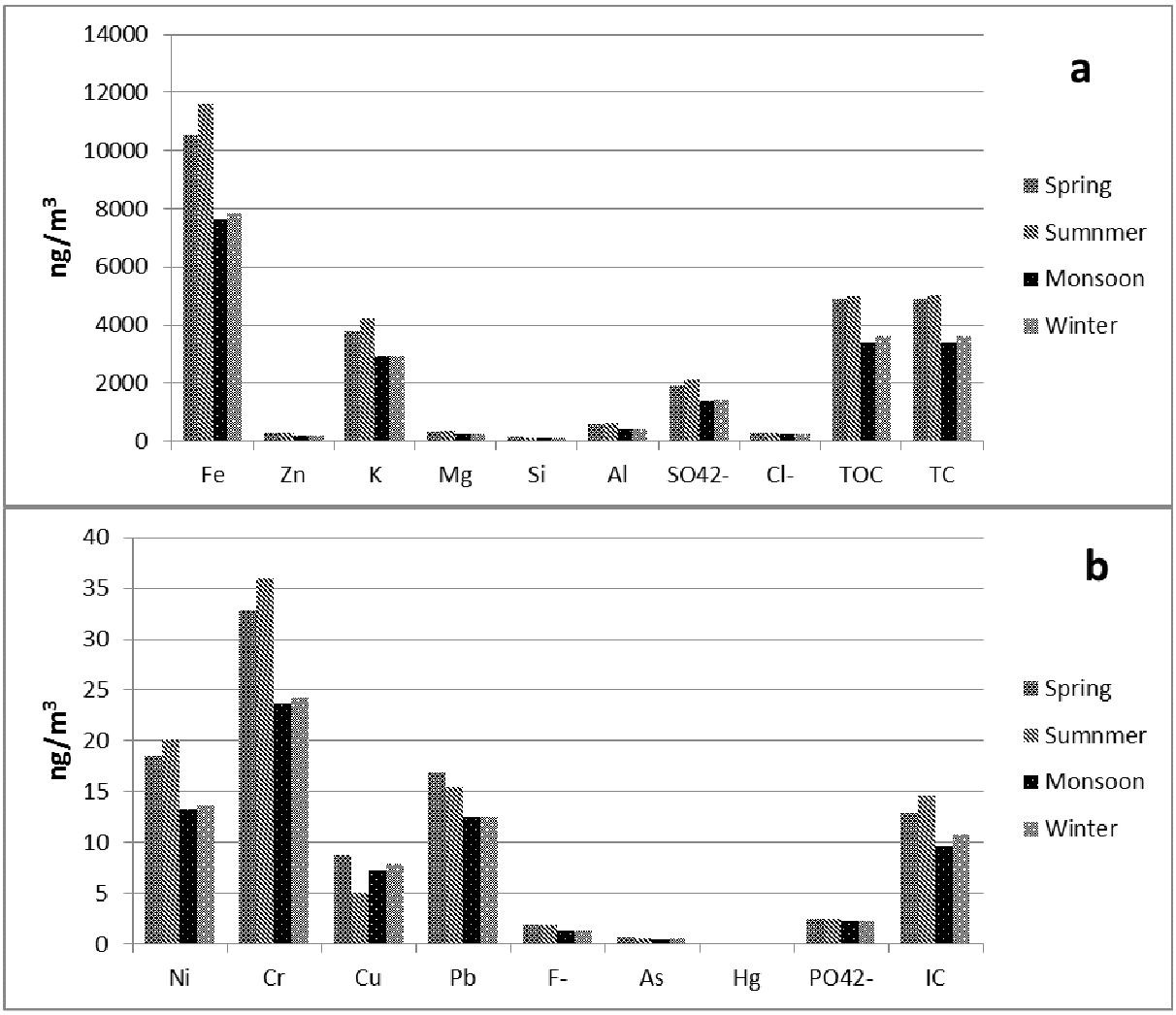


Figure 4.1. Seasonal Variations of major elemental and anionic composition in PM_{10} a) concentration ranges 100-12000 ng/m^3 b) concentration ranges 0-40 ng/m^3

In this context it is emphasized that winter and spring season is characterized by calm wind conditions, moderate temperature and scanty rainfall. The major natural sources will be less active during winter and spring seasons. Similarly, the wet removal of aerosols is also less efficient during winter and spring. But due to lower mixing heights and inversion effect the concentration of PM were increased as compared to monsoon. Also scanty rainfall in the winter and spring seasons and consequent longer detention time of aerosols increase the atmospheric concentrations of aerosol and its metallic and anionic mass concentrations.

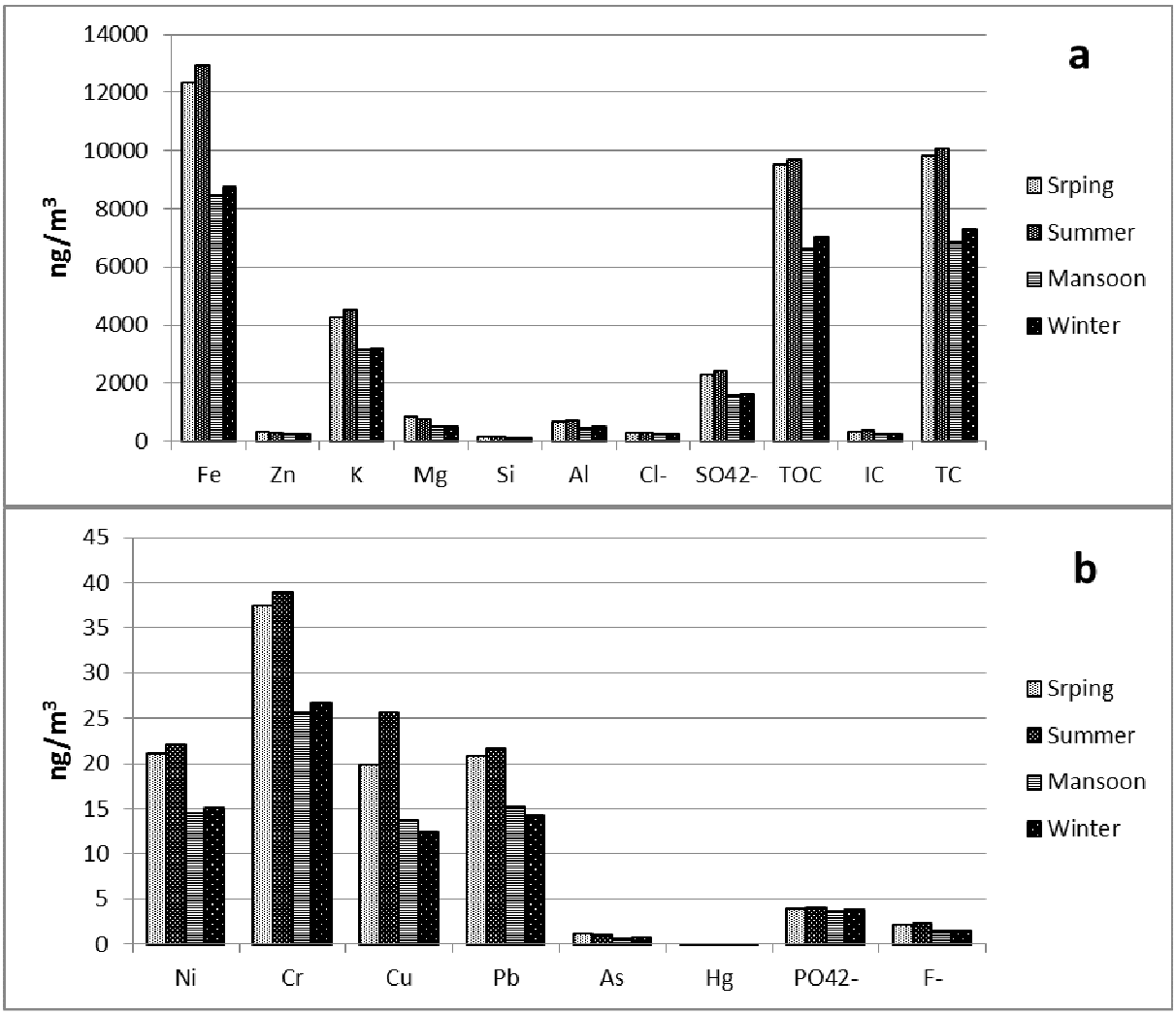


Figure 4.2. Seasonal Variations of major elemental and anionic composition in TSP a) concentration ranges 100-14000 ng/m^3 b) concentration ranges 0-40 ng/m^3

Under the influence of moderately high wind and convective mixing during summer, mineral dust derived from the disturbed soils is lifted in the atmosphere resulting suspension and re-suspension causing highest concentration of PM during this season. Moreover the wind blowing across the city carries with it the dust emitted from cluster of sponge iron plants located around Rourkela in Sundarghad district of Odisha. This windblown dust is being accumulated in Rourkela city because of the hill area that is present across it (Figure 3.2).

4.3 CORRELATION ANALYSIS

Spearman rank correlation analysis has been performed between measured aerosol and its metallic and anionic species to investigate the relationships between them using software IBM SPSS 20. The Spearman rank correlation coefficient (*r*) measures the relationship between two variables, the extent to which one variable increases as the other also increases, regardless of the numerical size of the increase. This r between two parameters is calculated by equation (4.1). The term D is the difference of the rank of two variables, each with N number of data set.

$$r = 1 - \frac{6\sum D^2}{N^3 - N} \tag{4.1}$$

The coarse and fine mode fraction of particulate matter present in air is either directly released into the atmosphere by industries, or derived through weathering of rocks and other surfaces. Various publications concerned with ambient air pollution simply refer to soil- and rock-derived dust as ‘‘crustal particles’’, with little consideration given to how much of a local geological signature might be recognized from this particle subgroup (Moreno et al. 2004). Based on specific gravity and the type of metal ions present, crustal particles can easily be divided into two groups, i.e., mafic and felsic silicate minerals (Marshak 2009). Thus, Spearman’s rank correlation analysis is carried out on PM compositions to characterize their metallic and anionic species with regard to their geological origins. The results of spearman rank correlation study between chemical constituents of PM_{10} (table 4.4) shows that correlation between Ni-Cu, Ni-Pb, Fe-F^-, Cr-K, Cu-F^-, Al-Pb, Mg-SO_4^{2-} and Si-Al were statistically significant. Out of these significant correlations Ni-Pb, Ni-Cu and Mg-SO_4^{2-} were negative indicating an inverse correlation between them which also suggests different sources between them. A negative correlation between two elements suggests that there is a trend that increase in

concentration of one element is simultaneously happening with decrease in concentration of other element. For example, in case of Ni-Cu, whenever fraction of Ni increased in PM_{10}, it was observed that the concentration of Cu is decreasing. One should remember that it is not a case of cause and effect i.e. the increase in Ni concentrations is causing the decrease in Cu concentration. Rather it can be depicted that those two elements were originated from different sources for sure. While positive correlations between Ni-Cu, Cr-K, Al-Pb and Si- Al can be explained by the fact that they can have common sources, the positive correlation between Fe-F^- and Cu-F^- is an anomaly that has been observed during the study. Earth crust is one of the major sources for these three constituents i.e. Fe, Cu and F^-. The results of spearman's rank correlation study between the constituents of TSP were shown in table 4.5. Magnesium is one such element that has shown strong correlation with highest number of species. This explains that the TSP has geological origins of silicate minerals such as biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) where magnesium comes along with Si, Al, K, Fe, F. Correlation between Mg and As indicate that minerals like adelite ($CaMgAsO_4OH$) and Brassite ($Mg(AsO_3OH)_4(H_2O)$). The correlation between Mg and SO_4^{2-} indicate the presence of minerals like Boussinguatite ($(NH_4)_2Mg(SO_4)_26H_2O$) (Marshak 2009). In general all these correlations indicate that the origination of TSP is from both mafic and felsic silicate minerals. The higher concentrations of heavy metals may indicate that mafic silicate minerals are major contributors of TSP but it can be explained by the fact that the sampling area is surrounded by iron ores that generally contains mafic minerals in higher proportions. From table 4.5 it can also be observed that Si also has shown significant correlation with other elements and anions, which in general supports the theory that the TSP is majorly originated from the silicate minerals of soils, ores and rocks. The processing of ores will enhance the weathering of soil contents in to the atmosphere.

Also, the solid waste released from the blast furnace will also contain so many trace minerals that are weathered into the atmosphere. The correlation between anions (Cl^-, SO_4^{2-}, F^- and PO_4^{2-}) and some of the cations is also predominant indicating that those anions and cations will be accruing in combinations as in silicate minerals. A negative correlation has been shown by mercury with anions and cations. This may be due to the adsorption capacity of minerals in general towards mercury. The coarse fractions of the minerals may be adsorbing the mercury present in atmosphere and were settling down (Melamed and da Luz 2006).

These correlation studies have given an insight to the source apportionment studies that were conducted in urban areas of Rourkela city. While using receptor models with unknown sources (PCA/APCS and PMF), contribution of factors to each of the elements present in particulate matter (PM) plays important role in identifying the source category. The process of identifying the sources is highly beneficiated from the knowledge of correlations between different elements. As explained above, correlations between elements/ ions whether they are positive or negative will indicate the commonality and individuality of the sources between them.

Table 4.4. Spearman rank Correlation matrix between elemental and anionic species present in PM_{10}.

	PM_{10}	Fe	Ni	Cr	Zn	K	Cu	Pb	Mg	Si	Al	As	Hg	Cl^-	PO_4^{2-}	F^-	SO_4^{-2}
PM_{10}	1.000	0.085	0.085	0.093	-0.065	-0.004	0.073	-0.184	0.082	0.112	-0.283**	-0.030	0.098	-0.063	0.095	0.125	0.044
Fe		1.000	-0.320**	0.131	-0.103	0.124	-0.093	0.057	0.013	0.115	-0.030	0.095	0.089	-0.030	-0.105	0.267**	0.142
Ni			1.000	0.029	-0.015	0.000	-0.262**	-0.213*	-0.161	0.011	0.095	-0.105	-0.030	0.095	0.082	0.098	-0.063
Cr				1.000	0.007	0.213*	0.019	0.089	-0.006	0.005	-0.105	-0.015	0.095	-0.105	0.013	-0.014	-0.123
Zn					1.000	-0.102	0.086	0.104	0.067	-0.190	-0.015	0.156	-0.105	-0.015	-0.161	-0.023	0.012
K						1.000	-0.020	-0.024	0.216*	0.017	0.156	-0.017	-0.015	0.156	-0.006	-0.069	-0.008
Cu							1.000	-0.081	0.007	0.008	-0.017	0.098	0.156	-0.017	0.067	0.253**	-0.004
Pb								1.000	-0.157	-0.058	0.247**	-0.014	-0.017	0.095	0.098	-0.158	-0.058
Mg									1.000	-0.154	-0.168	-0.023	0.098	-0.105	-0.014	-0.081	-0.251**
Si										1.000	0.256**	-0.069	-0.014	0.098	-0.023	-0.019	0.188
Al											1.000	0.089	-0.023	-0.014	-0.069	-0.083	-0.125
As												1.000	-0.069	-0.023	0.089	0.095	0.089
Hg													1.000	-0.069	0.095	-0.105	0.095
Cl^-														1.000	-0.105	0.089	-0.105
PO_4^{2-}															1.000	0.089	0.089
F^-																1.000	0.191
SO_4^{-2}																	1.000

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.5. Spearman rank Correlation matrix between elemental and anionic species present in TSP.

	TSP	Fe	Ni	Cr	Zn	K	Cu	Pb	Mg	Si	Al	As	Hg	Cl^-	PO_4^{2-}	F^-	SO_4^{2-}
TSP	1.000	-.121	-.093	.462	-.231	-.148	.401	-.231	-.066	-.187	-.082	.319	.269	-.126	.297	-.082	-.099
Fe		1.000	-.379	.132	.209	.577*	.027	-.132	-.154	-.275	-.247	-.352	.148	-.462	-.604*	-.247	-.225
Ni			1.000	-.055	-.044	-.473	-.379	-.077	.429	.346	.407	.341	.038	.566*	.346	.407	.396
Cr				1.000	.115	.335	-.258	-.110	.060	-.060	.022	.264	.231	-.143	.231	.022	.005
Zn					1.000	.291	.231	-.407	-.005	-.088	-.055	-.319	0.000	.099	-.236	-.055	-.027
K						1.000	.165	-.462	.044	-.011	.077	-.093	-.440	-.341	-.148	.077	.115
Cu							1.000	-.533	-.027	-.110	.022	.044	-.368	.038	.110	.022	.049
Pb								1.000	-.516	-.396	-.489	-.253	.505	-.363	-.203	-.489	-.527
Mg									1.000	.951**	.951**	.742**	-.555*	.665*	.516	.951**	.940**
Si										1.000	.940**	.654*	-.549	.665*	.489	.940**	.929**
Al											1.000	.758**	-.593*	.692**	.654*	1.000**	.995**
As												1.000	-.412	.478	.863**	.758**	.714**
Hg													1.000	-.341	-.363	-.593*	-.621*
Cl^-														1.000	.577*	.692**	.698**
PO_4^{2-}															1.000	.654*	.621*
F^-																1.000	.995**
SO_4^{2-}																	1.000

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

4.4 ENRICHMENT FACTOR ANALYSIS

The ratios of atmospheric concentration of elements to a reference element are compared to the same ratios in geological or marine material. Differences are explained in terms of anthropogenic sources. Heavy metal enrichments are usually attributed to industrial emitters (Reimann and Caritat 2000). Enrichment factor (EF) calculations are used as a screening tool to separate a reference source from all other sources (Chen et al. 2008; Duan et al. 2006; Haritash and Kaushik 2007; Saldarriaga-Noreña et al. 2009). Enrichment factors (EF_{crust}) of metals in the urban aerosols were calculated according to Wedepohl, 1971. The usefulness of EF calculations is based on the assumption that similar elemental ratios (ratio=1) found between elements in airborne samples and in reference material suggest reference material as a likely source. Given the inaccuracies in characterizing reference materials, an EF value of 10 is selected as a baseline (Zhang et al. 2012). The EF values greater than 10 suggest a source other than the reference material. The reference element is chosen on the basis that the reference material (earth crust) will be the major or likely the only source of that particular element. The average contribution of individual elements to their total mass in PM_{10}, TSP and the earth crust are shown in figure 4.3. From figure 4.3 it can be observed that Si is a major component in the composition of earth crust where as it has almost negligible contribution in aerosols. It can be assumed that the minute contribution of Si in aerosol is majorly or only due to the earth crust. Thus Si is considered to be the reference element for the enrichment factor (EF_{crust}) calculations. The EF_{crust} for the metal *X* relative to the earth crust with reference to Si is defined in equation (4.2).

$$EF_{crust} = \frac{\left(X/Si\right)_{air}}{\left(X/Si\right)_{crust}} \qquad (4.2)$$

Where *X* is the concentration of the element of interest, and *Si* is the concentration of the reference element. In general, the global/continental earth-crust elemental composition is used for the calculation of enrichment factor. Enrichment factor indicates the enrichment of an element in the atmosphere as compared to the normal abundance in the earth crust. This enrichment may be due to geological and/or anthropogenic activities. Thus, using global earth crust values will be suitable rather than using the local earth crust values for the calculation of enrichment factors. Average global elemental composition of the continental upper earth crust was taken from(Hans Wedepohl 1995).

Enrichment factors of different trace metal ions are presented in figure 4.4. All the trace metals considered other than Si are enriched significantly with Pb, Zn and K being predominant. Alkali metals and zinc are known to be the major elements in fine particles released from biomass combustion (Steinvall et al. 2012). This is explained by the relative high vapor pressure of some of their species in the combustion process, causing a release of volatilized inorganic matter that subsequently condensate and forms fine aerosol particles when the flue gases are cooled in the process (Steinvall et al. 2012).

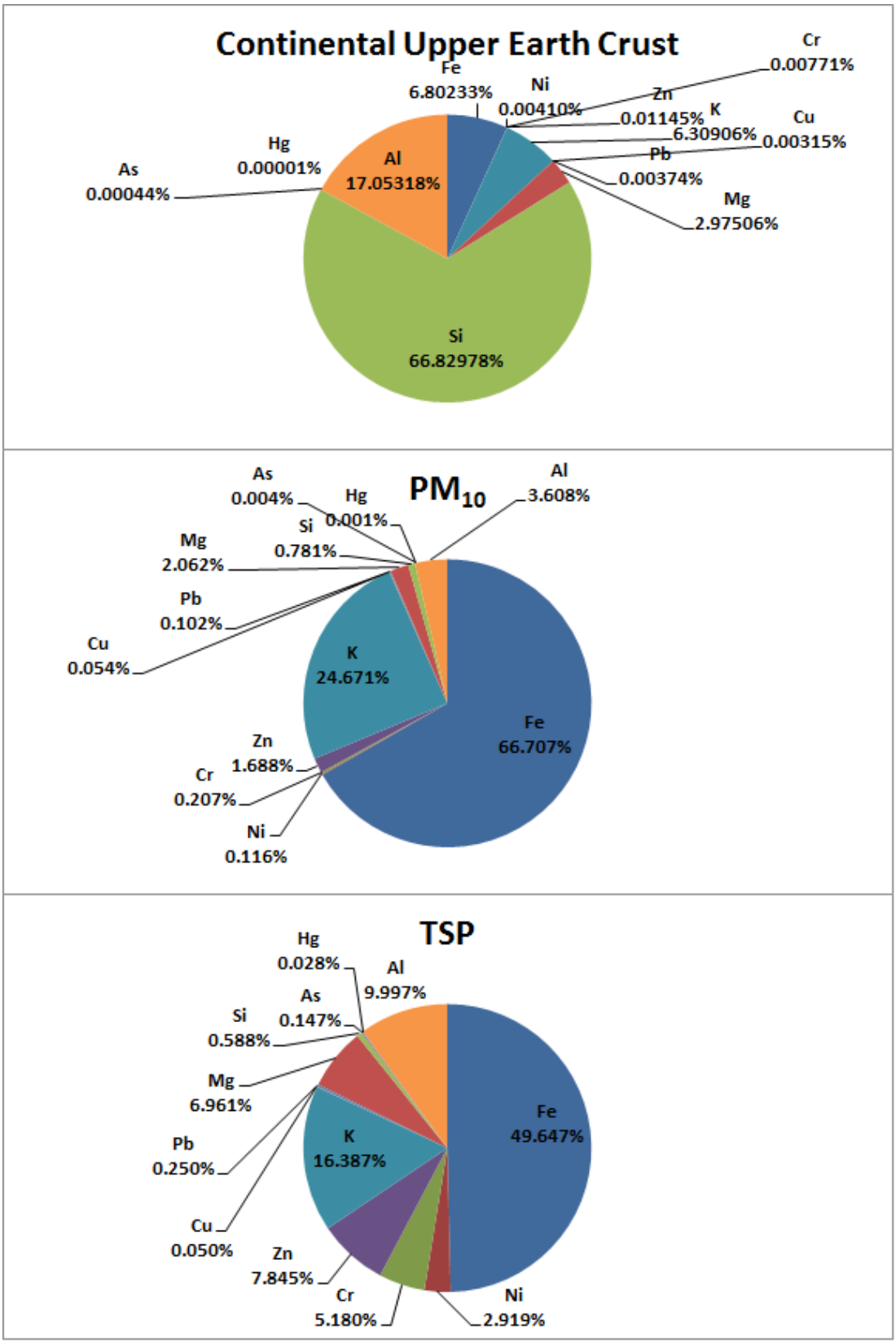


Figure 4.3. Percentage contributions of different elements in PM_{10}, TSP and Earth's crust.

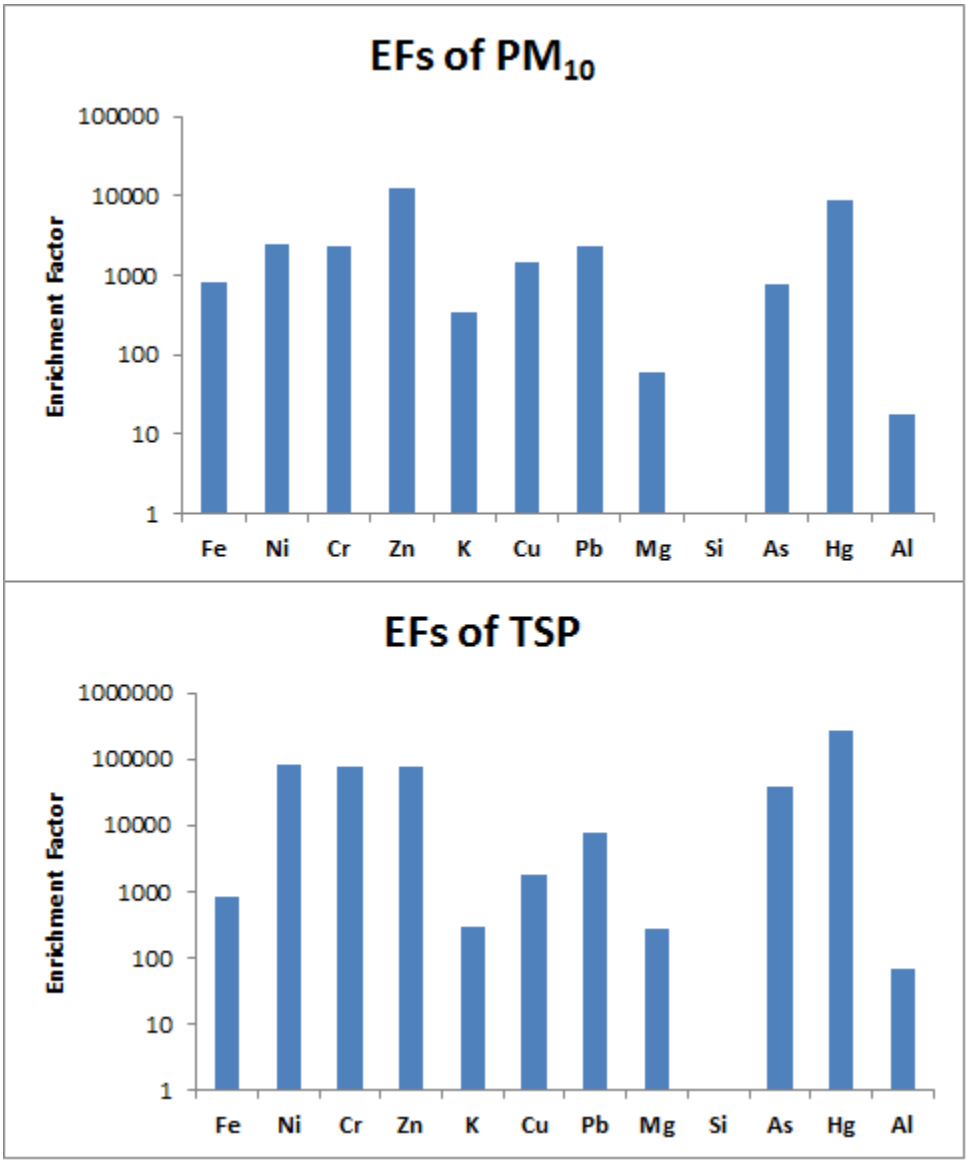


Figure 4.4. Enrichment factors for different elements of PM_{10} and TSP.

Zinc is the major trace element in most biomass fuels and found in surprisingly high concentrations (1- 10 mass %) in the particulate matter formed during combustion of these fuels. So the enrichment of Zn and K can be related to the biomass combustion of municipal waste and biomass fuels used by people in rural areas like Jagda and Jhirpani surrounding the city. Lead is enriched due to vehicular emissions. Metals such as Fe, Al, Ni, Mg and Si are enriched due to mining, ore processing and industrial activities (Kothai et al. 2011; Yadav 2014). Thus it can be

concluded that all the metal ions considered in this study have a non-crustal i.e. anthropogenic origin. Other studies conducted across India also have shown similar results. A study conducted by Kothai and others at Navi Mumbai, India has shown significant enrichment in case of Ni, Zn, Pb, As, Cr (Kothai et al. 2011). Sudheer and Rengarajan have shown that metals like Fe, Cr, Ni, Cu, Zn and Pb were significantly enriched in the city of Ahmedabad located in western India (Sudheer and Rengarajan 2012). In both the cases one of the most enriched elements are Zn and Pb as is the scenario in the present study. This enrichment study pioneered in identifying the sources in receptor modeling with unknown sources. It also helped in choosing different source profiles for chemical mass balance (CMB) modeling. On the basis of enrichment factor, sources like road dust, biomass burning, vehicular emissions, diesel exhaust and other industrial sources were chosen for the CMB modeling.

CHAPTER 5- SOURCE APPORTIONMENT

5 SOURCE APPORTIONMENT

Encompassing air quality information investigations and receptor systems are an undeniably imperative part of viable air quality management systems. Distinguishing the emissions between anthropogenic and natural causes along with their influences on air pollution helps in recognizing and evaluating the important sources to be controlled. The utilization of climatic compositional information for the recognizable proof and division of sources has been continuous for over 40 years. Starting in the 1960s, it was perceived that data analysis methods could be connected to data and resolve combination of constituents that signify sources. In the late 1970s, these data analytical instruments came to be called Receptor Models.

The first reported receptor modeling in the literature had been developed in the social sciences for interpreting large data sets using factor analysis. Principal component analysis (PCA) has been used in that study with several types of axis rotations to examine particle composition data collected by the National Air Sampling Network (NASN) during 1957–61 in 30 U.S. cities (Blifford and Meeker 1967). Similar study has been conducted in 12 West German cities along with air quality data of Detroit in 1968 using factor analysis methods(Prinz and Stratmann 1968). In both cases, they found solutions that yielded readily interpretable results. In later years a concept of atmospheric mass balance model was suggested (Miller et al. 1972; Winchester and Nifong 1971). Specific elements called ‘tracer elements’ were linked in these methods with different source types while developing a mass balance for airborne particles.

Afterwards, a least–square fit which uses more chemical species than sources to provide estimates of the mass contributions of the sources has been used (Friedlander 1973). Ever since, a number of other applications of these approaches have been made in a wide variety of locations and extensive libraries of source profiles have been developed to be used in receptor models.

Receptor models give the hypothetical and numerical structure for evaluating source contributions at that receptor. There are two fundamental classes of receptor models:

1. Known sources (e.g. Chemical Mass Balance); and
2. Unknown sources (e.g. Principal Component Analysis and Positive Matrix Factorization).

In the first type, a regression method is utilized to match chemical profiles in measured ambient particulate matter to those in emissions from potential sources. Chemical Mass Balance (CMB) requires an earlier knowledge of real sources and their discharge attributes in the study area. CMB modeling delivers the resources by which one can estimate contribution rate of each emission source to the measured pollutant concentration. These statistical techniques are utilized for distinguishing and evaluating the contribution of vital emission sources.

Source apportionment with unknown sources requires only ambient data in source apportionment performance. In these models, the internal variability of the data will determine factor profiles and their contributions to each sample. These factor profiles are connected back to particular sources, for example, combustion or diesel emissions. At the very least, a hundred or more specimens from numerous areas and/or one area over quite a time period are required for this sort of receptor modeling.

Source apportionment studies include the surrounding scrutiny and estimation of air particles or gasses, trialed by laboratory investigations to discrete and recognize the constituents

of the samples gathered by their chemical configuration. Chemical speciation monitoring helps researchers to comprehend the properties of the airborne particulate matter at the receptor site(s) and to recognize the emission sources, including potential sources which are not promptly distinguished in preliminary emission inventories, for example, cooking fires and airborne particles transported over long separations. Furthermore, the examinations evaluate the commitment of known emission sources and can approve and enhance the emission inventory itself.

Objectives of source apportionment studies can include:

- To quantitatively relate emissions to the characteristics of targeted aerosols at a specific receptor site.
- To assess the viability of control methodologies after some time.
- To enhance and approve emission inventories by deciding real sources of air pollutants
- Fortifying environmental management, especially at territorial and nearby levels.
- Upgrade the linkages between particular emission sources and encompassing air quality.
- Give directions to the utilization of source models.
- Assessing and enhancing source model results.
- Providing data to support the reduction of emissions through coordinated systems.

Progressively, source apportionment analyses are being utilized as a moderately accurate, rapid, and financially savvy method for distinguishing and focusing on sources and their relative contributions to the total pollution load. This scientific information helps air quality modelers as well as policy and decision makers.

The data obtained from source apportionment studies provides policy and decision makers with practical tools to identify and quantify different sources of air pollution, increasing

their ability to put in place effective policy and regulatory measures and control strategies to reduce air pollution to acceptable levels. Additionally, co-benefits can be realized. For example, source apportionment studies targeting specific air pollutants can also be used to assess climatic impacts, identify clean energy measures and greenhouse gas emission reduction strategies.

5.1 CHEMICAL MASS BALANCE MODELS

The fundamental principle of chemical mass balance model is the mass conservation that can be used to identify and apportion sources of airborne particulate matter in the atmosphere (Gupta et al., 2007). According to the assumptions of CMB, chemical species do not react with each other. It is necessary to measure source profiles.

Chemical mass balance (CMB version 8.2) modeling approach using multiple linear least–squares regression has been used to identify the probable sources of aerosol in the study area.

Mass balance equation for CMB of all *m* chemical species in the *n* samples as contributed from *p* independent sources is given by equation (5.1)(Miller et al. 1972).

$$X_{ij} = \sum_{k=1}^{p} c_{ik} S_{kj} \tag{5.1}$$

where X_{ij} is the i^{th} species concentration measured in the j^{th} sample at the receptor site, $i = 1,2,...,m$ and $j = 1,2,...,n$; c_{ik} is the fractional composition for the i^{th} chemical species from the k^{th} source, and S_{kj} is the airborne mass concentration of species from the source k contributing to the j^{th} sample.

With the knowledge of number and nature of sources in receptor region, the mass contribution of each source to each sample can be calculated (Miller et al., 1972; Watson, 1979).

Miller et al. (1972) modified equation (5.1) to explicitly include changes in composition of the source material while in transit to the receptor as given by equation (5.2).

$$X_{ij} = \sum_{p=1}^{k} \alpha_{ik} c'_{ik} S_{kj} \tag{5.2}$$

Where α_{ik} is the coefficient of fractionation so that if c'_{ik} were the composition of the particles as emitted by the source

In order to obtain a quantitative measure of the contributions of various sources receptor modeling using the classical CMB 8.2 package has been carried out. This is a well-tested package and it uses as inputs source profiles which are characteristic of the emissions of various sources. CMB also accounts for changes in composition of the source material in transit to the receptor; although it requires source profiles to account for these changes (Srivastava 2004).

An emission survey has been carried out to identify potential contributors to urban aerosols in Rourkela. The main focus of the survey is a 10 km × 10 km area around each monitoring site. This survey identified various sources in the present urban area, including a steel plant, cement factory, fertilizer factory, domestic utilities, and solid waste burning sites. For the purpose of source apportionment, the main sources of Rourkela were classified into three groups: crustal related, combustion related, and industrial related sources. Soil dust, unpaved/paved road dust, dust from construction or aggregate processing, as well as fugitive dust emissions from the fertilizer plant belong to the first group. Wood combustion, fuel oil combustion, LPG combustion, solid waste burning and medical waste incineration belong to the second group. While industrial manufacturing, industrial diesel generators, cement kiln, average steel production, basic oxygen furnace and iron ore dust from sintering plants represent the third

group. Diesel exhaust also was included, since much heavy transportation takes place within the study area.

Table 5.1. Source profile data for paved road dust and soil dust at Rourkela.

Species	Paved Road Dust		Soil Dust	
	% mass	Uncertainty	% mass	Uncertainty
Fe	12.0336	1.1320	19.4451	1.8292
Ni	0.0104	0.0010	0.0513	0.0048
Cr	0.0344	0.0032	0.0533	0.0050
Zn	0.1507	0.0142	0.3122	0.0294
K	0.9528	0.0896	0.6712	0.0631
Cu	0.0216	0.0020	0.0194	0.0018
Pb	0.0492	0.0046	0.0707	0.0067
Mg	1.1526	0.1084	1.3068	0.1229
Si	0.1037	0.0098	0.5202	0.0489
As	0.0117	0.0011	0.0537	0.0051
Hg	0.0145	0.0014	0.0160	0.0015
Al	0.1336	0.0126	0.3242	0.0305
F^-	0.0150	0.0014	0.3678	0.0346
SO_4^{2-}	0.6910	0.0650	0.4652	0.0438
Cl^-	0.3804	0.0358	0.3974	0.0374
PO_4^{3-}	0.0407	0.0038	0.0144	0.0014
TOC	14.0854	1.3250	21.4001	2.0132
IC	1.0259	0.0965	0.9179	0.0863
TC	15.1113	1.4216	22.3180	2.0995

Most source profiles and their uncertainties for these local sources were obtained from the studies of the Central Pollution Control Board (CPCB) (Patil et al., 2013; Sethi and Rashmi, 2008a) or matched with profiles in the US EPA SPECIATE 4.4 database.

Soil dust and paved road dust source profiles for TSP were developed in the present study. The mass percentage of different chemical species and their uncertainty values of road dust and soil dust of Rourkela are summarized in Table 5.1. From the table it is clear that iron is predominating species among the elements whereas sulfate and chloride are abundant in both paved road dust and soil dust samples. Organic carbon and total carbon are also present in abundance which can be attributed to the vehicular emissions and anthropogenic activities.

Table 5.2 summarizes these source profiles and their respective databases. The SPECIATE 4.4 database gave the profiles for vehicular sources along with some other stationary sources that are not available in non vehicular sources database given by CPCB (Patil et al., 2013; Sethi and Rashmi, 2008b). CMB requires the use of daily data that was observed. Hence, for each day the measured concentrations from speciation analysis consisting of ions, elements and carbon content were used to estimate the various source contributions. The primary emission survey gave an insight into the various sources present in an area.

This was used to identify the sources as inputs for the CMB. The corresponding profiles were given as input to the CMB in the required format and so were the receptor values. The performance of numerical algorithm depends on the uncertainties involved in the source profiles and receptor concentrations. The uncertainties of SPECIATE and CPCB profiles are well defined. However, for the soil dust and road dust profiles standard deviations (SD) for the total number of soil dust and road dust samples were used as uncertainty. The uncertainties of receptor concentrations were calculated and fed into the CMB software package. For both PM_{10} and TSP

the results of the analysis are presented below in a graphical form. The pie diagram gives us insight into the average contribution over the entire monitoring period for a particular season and site. Here the contributions of each source were determined and then average it over no of days.

Table 5.2. Summary of different source profiles considered for CMB and their respective databases.

Source	**Database**
Soil Dust	Source Profile Data of soil collected at Rourkela
Paved Road Dust	Source Profile Data of paved road dust collected at Rourkela
Unpaved Road Dust	Source Profiles –. CPCB
Wood Combustion	Source Profiles –. CPCB.
Coal Combustion (Stoves)	Source Profiles –. CPCB
Fuel Oil Combustion (Boilers)	Source Profiles –. CPCB.
Construction and Aggregate Processing	Source Profiles –. CPCB
Industrial Diesel Generators	Source Profiles –. CPCB.
Solid Waste Burning	Source Profiles –. CPCB
Medical Waste Incineration	Source Profiles –. CPCB.
LPG Combustion	Source Profiles –. CPCB
Fugitive Dust Emission (Fertilizer Plant)	Source Profiles –. CPCB.
Steel Production (General)	SPECIATE 4.4, USEPA
Blast Furnace	SPECIATE 4.4, USEPA
Coke Oven	SPECIATE 4.4, USEPA
Diesel Exhaust	SPECIATE 4.4, USEPA

Results of the CMB model summarized that there is a dominance of emission from steel production in both PM_{10} and TSP with contributions of 32.5% and 25.61%, respectively as shown in figures 5.1 and 5.2. Diesel exhaust is the second largest contributor to PM_{10} aerosol (25.67%) which indicates the dominance of transportation in the contribution of PM_{10} aerosol

data. Presence of all the sampling sites in proximity of the major roads is one of the reasons for higher diesel exhaust fraction in PM_{10}. Along with the heavy vehicles, diesel generators present in the Udit nagar area also played an important role in this contribution. Paved road dust is the third largest contributor with 16.24% followed by soil dust as fourth largest contributor with 11.74% of PM_{10} aerosol. These road and soil dusts are in the ambient air by the re-suspension of dust particulates. A significant contribution of 6.12% was observed for PM_{10} from basic oxygen furnace of steel plant. In general basic oxygen furnace (BOF) is an integral part of steel production. Thus this source profile should show some collinearity with source profiles of average steel production. But it has been found that the collinearity is bare minimum between these two profiles which was confirmed by the sensitivity tests conducted on CMB model (Table 5.3). The reason behind this lies in the profiles that were chosen from the SPECIATE database. A composite source profile was chosen for average steel production with profile number 9000430 which represents the PM sizes up to 30µm. This average profile has been developed from original profiles representing the source category group 303009xx in the SPEACIATE database. The source category group 303009xx include source profile numbers from 30300901 to 30300936 which represent different processes involved in the steel making out of which four profiles were related to BOF (30300913- BOF: open hood stock, 14- BOF: Closed hood stock, 16- Charging BOF, 17- Tapping BOF). But none of those four profiles were representing the basic oxygen furnace as a whole. So the source profile that has been chosen for basic oxygen furnace in a detailed source profile number 2830710 in SPECIATE database. Thus a minimum amount of collinearity was found between the profiles 9000430 (Average Steel Production) and 2830710 (Basic Oxygen Furnace). Solid waste burning like municipal waste burning including

incineration and wood burning also contributed about 2.39% to the PM_{10} aerosol. All other sources that have been considered have shown 5.34% contribution to PM_{10}.

For TSP the dominated source was steel production accounting for 25.61% followed by paved road dust (19.24%), diesel exhaust (17.03%), soil dust (10.47%), construction and aggregate processing (8.25%) and solid waste burning (3.41%). All the remaining sources have contributed 15.99% to TSP. As compared to PM_{10}, the contribution of paved road dust is significantly higher whereas diesel exhaust is lower in TSP. This indicates that the re-suspended road dust has higher percentage of coarse PM whereas vehicular emissions have higher percentage of finer fraction of PM. Soil dust contribution in TSP and PM_{10} are not very different. But in case of TSP, construction and aggregate processing has shown a significant contribution of 8.25%. This may be mainly due to the construction works that were going on at both Udit nagar and NIT Rourkela. It also designates that the construction works in general produces coarser fraction than finer fractions of PM

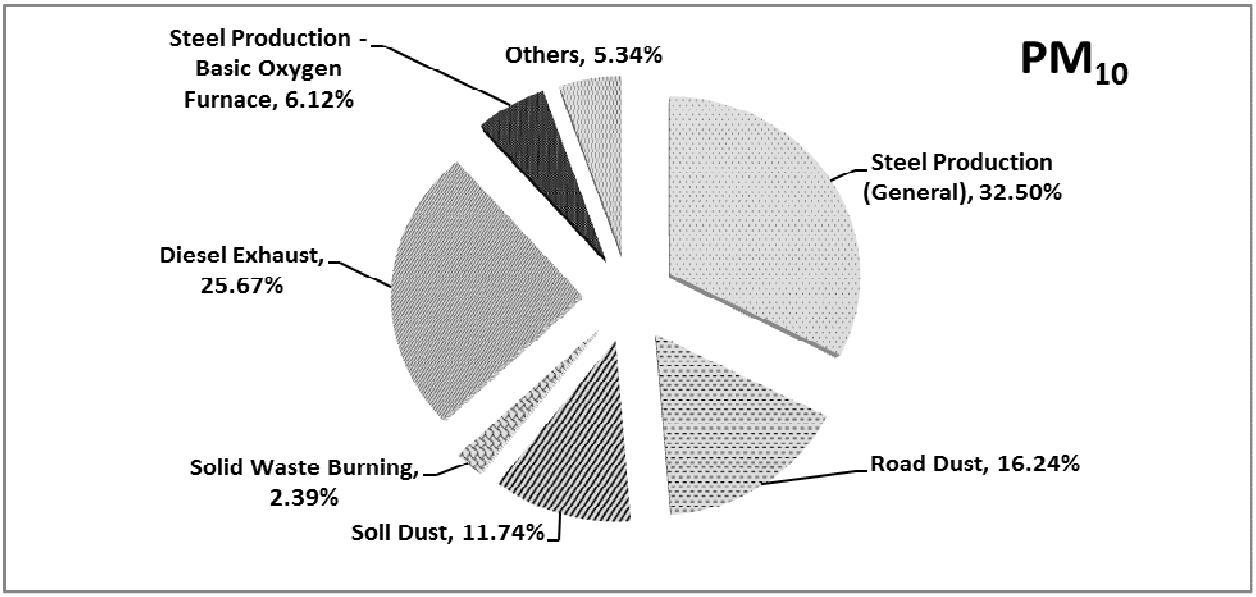


Figure 5.1. Contribution of sources to PM_{10} aerosol determined by CMB model at Rourkela

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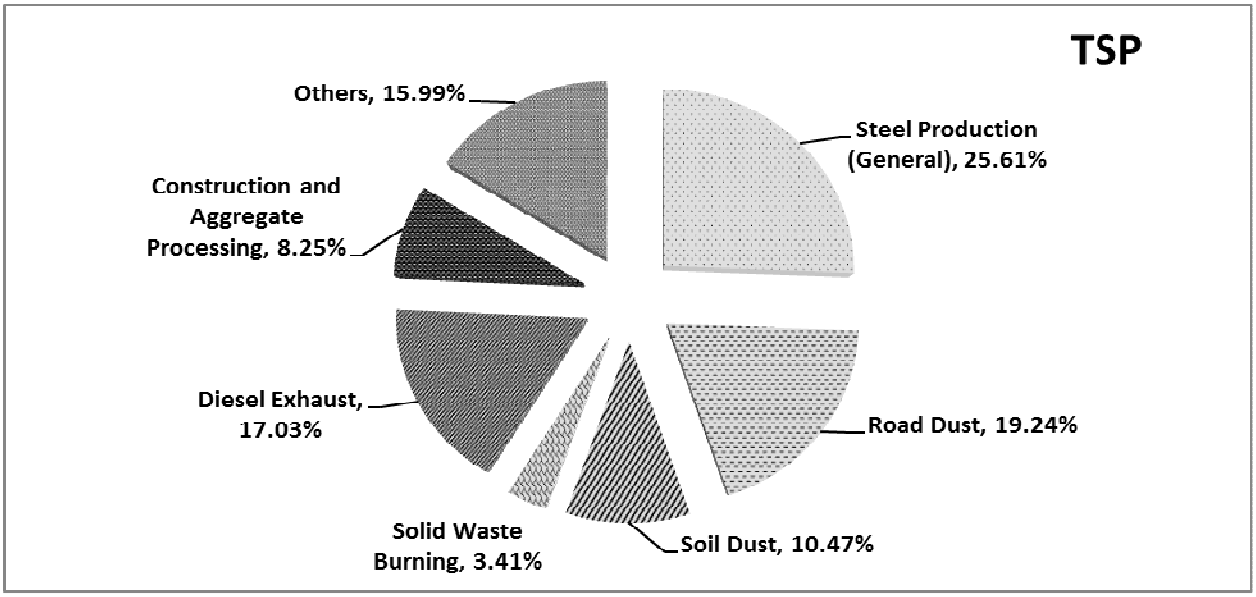

Figure 5.2. Contribution of sources to TSP aerosol determined by CMB model at Rourkela

5.1.1 CMB MODEL PERFORMANCE MEASURES

The accuracy of CMB source contribution estimates is difficult to establish because they are based on a least squares linear regression (Gupta et al., 2007). Hence, the coefficient of determination (r^2), chi-square (χ^2), and percent mass values were used to evaluate the source apportionment. The r^2 is the fraction of the variance in the measured concentrations that is explained by the variance in the calculated species concentrations. The r^2 value ranges from 0 to 1.0. The closer the value of r^2 towards 1.0, the better the source contribution estimates explain the measured concentrations. The chi-square value (χ^2) is a weighted sum of squares of the difference between calculated and measured fitting species concentrations and should be equal to 1 for a very good fit. Values between 1 and 2 are acceptable and values greater than 4 indicate that one or more species concentrations are not well explained by source contribution estimates. Percent mass is the percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration.

Table 5.3. Sensitivity test results for PM_{10} and TSP over the study period.

Source Profile	PM_{10}				TSP			
	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**	**Trial 1**	**Trial 2**	**Trial 3**	**Trial 4**
Soil Dust	**14.67**	14.67	23.18	23.66	11.97	9.20	**15.38**	23.66
Paved Road Dust	**12.50**	12.08	15.89	13.09	5.56	3.23	**16.87**	13.09
Unpaved Road Dust	**7.56**	7.56	4.25	6.81	2.22	3.18	**9.79**	6.81
Wood Combustion	**NC**	12.62	11.82	12.08	12.67	13.12	**0.97**	12.08
Coal Combustion (Stoves)	**1.50**	1.80	NC	NC	7.44	7.96	**5.06**	NC
Fuel Oil Combustion (Boilers)	**NC**	NC	1.97	NC	NC	NC	**NC**	NC
LPG Combustion	**NC**	8.93	8.62	9.10	8.36	9.16	**NC**	9.10
Solid Waste Burning	**3.00**	2.45	9.63	11.07	14.13	13.30	**4.75**	11.07
Medical Waste Incineration	**NC**	NC	NC	NC	3.27	4.23	**NC**	NC
Construction and Aggregate Processing	**1.59**	2.79	8.88	7.91	6.08	4.32	**7.41**	7.91
Industrial Diesel Generators	**NC**	NC	13.93	5.02	NC	NC	**NC**	5.02
Fugitive Dust Emission (Fertilizer Plant)	**NC**	-6.33	8.90	8.39	8.08	6.58	**3.77**	8.39
Coke Oven	**NC**	-0.74	1.08	1.49	NC		**0.85**	1.49
Industrial Manufacturing	**5.79**	9.54	5.02	4.59	10.23	11.84	**8.95**	4.59
Diesel Exhaust	**32.00**	32.52		9.21	13.32	12.50	**22.81**	9.21
Cement Kiln (Coal-Fired)	**NC**	8.88	7.85	8.81	5.52	6.21	**NC**	8.81
Steel Production (Average)	**40.00**	37.23	36.24	NC	28.43	NC	**35.24**	NC
Steel Production - Basic Oxygen Furnace	**7.70**	NC	NC	23.45	NC	24.10	**2.65**	23.45
Iron ore Dust -Sinter	**2.13**	NC	NC	4.33	6.20	6.36	**3.13**	4.33
Cumulative Contribution	**128.44**	143.99	157.26	149.00	143.50	135.29	**137.64**	149.00
Measured Concentration	**124.97**	124.97	124.97	124.97	139.36	139.36	**139.36**	139.36
Percentage Mass	**102.77**	115.22	125.84	119.23	102.97	97.08	**98.76**	106.92
R^2	**0.86**	0.74	0.72	0.81	0.69	0.63	**0.91**	0.73
$\chi 2$	**0.92**	0.64	0.82	1.12	1.85	1.57	**1.03**	0.95
Selected trial is highlighted in bold "NC" represents that the source profile in not considered in CMB modeling for that trial								

Percent mass ranging from 80% to 120% represent good fit to the data. EV-CMB (the effective variance weighted CMB) sensitivity tests were applied to data from several samples of both PM_{10} and TSP to evaluate the performance of different source profile combinations (Watson and Chow 2012). The initial source profile combination was modified in subsequent trials to examine changes in the standard contribution estimates (SCEs) and EV-CMB

performance measures. Often, only one profile in each source type could be included, since similar profiles resulted in collinearity, non-convergence, and/or negative source contributions. Some of the important results of these sensitivity tests for each season are presented in Table 5.3. The trial results highlighted in bold were the best results that were presented in figures 5.1 and 5.2. It can be seen that the selected trials fulfill most of the performance measures that were discussed above i.e. percentage mass is near to 100 and r^2 & χ^2 near to one.

5.2 PRINCIPAL COMPONENT ANALYSIS (PCA)

Principal component analysis (PCA) is a tool for analyzing structure in multivariate data sets. The great advantage of using PCA as a receptor model is that there is no need for a prior knowledge of emission inventories (Chio et al. 2004).

In this study, PCA will be applied to aerosols mass concentration data collected at different zones of study area. The species concentration matrix $[X_{(n\times m)}]$ with n rows (the number of analyzed chemical species) and m columns (the number of samples analyzed) will be standardized using the Z-score.

The PCA assumes that the total concentration of each species is made up of the sum of the contributions from each of *j* pollution sources for that species of aerosols (Thurston and Spengler 1985) as given by equation (5.3).

$$Z_{ik} = \sum_{j=1}^{p} W_{ij} P_{jk} \tag{5.3}$$

where P_{jk} is the j^{th} source value for observation *k*; *j=1,...,p*, the number of pollution sources influencing the data and W_{ij} is the coefficient matrix of the species *i* for source *j* (Thurston and Spengler 1985). Henry and Hidy (1979) found that equation (5.3) may be inverted, yielding in matrix terms. The principal component (PC) scoring matrix is derived so

that the first principal component (PC1) explains a large percent of the original variables' total variance as possible (Thurston and Spengler 1985). The coefficients for the second principal component (PC2) are, in turn, chosen so that it explains as large a percent of the remaining variance in the original variables (that is not explained by PC1), subject to the restriction that PC1 and PC2 are uncorrelated. In general, the coefficients for last PC explain as much of the remaining variance subject to the constraint that PC is uncorrelated with remaining PCs.

These principal component (PC) scores are correlated with their respective pollution sources impacting the site. Henry and Hidy (1979) showed that the regression of a dependent variable Y_k on the daily scores of components P_{jk} is given by the equation (5.4).

$$Y_k = \overline{Y} + \sum \varsigma_j P_{jk} \tag{5.4}$$

Where $\overline{Y}$ represents the mean of Y_k. If the dependent variable Y_k is the total mass in $\mu g/m^3$, then ς_j are the conversion coefficients of the non-dimensional PC score deviations into mass deviations from the mean source impact (Thurston and Spengler 1985).

The absolute zero PC score has subsequently been estimated for each PC by separately scoring an extra day. All the elemental concentrations are zero on that day. The estimates of the PC scores for each component at absolute zero are then used to estimate Absolute Principal Component Scores (APCS) for each component on each day by subtracting these scores from the scores of each day. Regressing aerosols mass data on these APCS will give estimates of the coefficients which convert the APCS into pollutant source mass contributions ($\mu g/m^3$) for each sampling period as given by equation (5.5).

$$M_k = \varsigma_0 + \sum_{j=1}^{p} \varsigma_j APCS_{jk}^{*} \tag{5.5}$$

where M_k is the particle mass recorded (in μg/m^3) during observation k, $APCS^*_{jk}$ is the rotated absolute component score for component j on observation k, $\varsigma_J APCS^*_{jk}$ is the particle mass contribution on observation k (in μg/m^3) made by the pollution source identified with component j, and ς_0 is the particle mass contribution (in μg/m^3) made by sources unaccounted for in the PCA (Thurston and Spengler 1985).

In the present research work applying PCA by using MATLAB (R2012b), source categories for PM_{10} and TSP constituents were identified. Varimax normalization rotation was applied to maximize (or minimize) the values of loading factors of each chemical species being analyzed in relation to each rotated principal components (Almeida et al. 2005; Oehme et al. 2006). These factors called principal components are acknowledged as emission source and/or chemical interaction. Each principal component may not have to represent one emission source, but rather more than one possible source. Before applying PCA, each individual sample has been scrutinized and those with remarkably extreme concentrations were identified as likely outliers. A sensitivity analysis has been conducted. The suspected outliers have been toned down using moving average filter several times until a stable PCA result was achieved. Component weights matrix obtained from PM_{10} samples are shown in table 5.4.

In this study, 19 variables were considered in the PCA with varimax rotation and a total of five components covering 89.34% of the data variance for PM_{10}. Factor loadings greater than 0.6 were considered to be significant in this study. The first component shows the representative loadings of Fe, Ni, K, Al, SO_4^{2-}, TOC and TC, and it explained 31.38% of the variance. This factor mainly associated with steel production, in general (Tsai et al. 2007). So first component (PC 1) is related to steel production. The second component explains a total of 20.2% data set variance and has factor loadings of Mg, Si, and Al, which are all soil minerals (Chelani et al.

2008; Khare and Baruah 2010a). So component two (PC 2) is associated with soil dust. Third component explains 18.13% of data and is related to Fe, Zn, Pb, TOC and TC. Zinc is normally considered as a marker for tire wear emission (Salvador et al. 2007). Lead is mainly associated with vehicular break wear or road dust emissions whereas TOC, TC, and iron may also be associated with the road dust emissions (Watson et al. 2002).

Table 5.4. Component weights matrix obtained from PM_{10} samples.

Variables	PC1	PC2	PC3	PC4	PC5
Fe	**0.72**	0.32	**0.67**	-0.49	**0.71**
Ni	**0.61**	-0.31	-0.47	0.25	-0.02
Cr	0.30	-0.09	0.18	0.30	-0.32
Zn	-0.43	-0.20	**0.78**	0.56	0.12
K	**0.63**	0.48	0.09	-0.12	-0.32
Cu	-0.33	**-0.69**	-0.10	-0.23	-0.23
Pb	0.48	0.27	**0.80**	0.43	0.51
Mg	-0.23	**0.76**	-0.21	-0.13	-0.31
Si	0.47	**0.88**	0.51	0.42	**0.83**
Al	**0.70**	**0.73**	-0.44	0.01	-0.32
As	-0.26	0.51	0.13	0.19	0.32
Hg	-0.11	0.08	0.16	0.32	0.31
Cl^-	-0.04	0.57	0.11	0.24	0.24
PO_4^{3-}	**-0.64**	0.14	0.47	-0.17	-0.17
F^-	0.53	-0.21	0.46	-0.25	-0.34
SO_4^{2-}	**0.87**	0.33	0.10	**0.67**	0.12
TOC	**0.68**	-0.44	**0.88**	**0.88**	0.31
IC	0.59	-0.32	-0.07	0.30	0.30
TC	**0.74**	0.39	**0.92**	**0.99**	0.47
Total Variance %	31.38	20.20	18.13	15.13	4.57

Fourth component explains 15.13% of the total variance and has loadings of sulphate, TOC, and TC. Sulphate is a secondary ion that is formed from gaseous precursor SO_2 (Perrone et al. 2010). The emission of TOC and TC is also associated with oil combustion that linked the emission of gaseous pollutants. Thus, the fourth component is oil combustion. Fifth component explained 4.57% of the total variance and has factor loading of iron and silicon. The study area is

surrounded by many mineral belts with rich ores. There is a constant activity of ore processing in these areas line crushing, concentrating and pelleting of ore before it is used for steel production. These activities contribute to the suspension and re-suspension of aerosol in the city enriched highly with iron and silicon. Thus, the fifth component represents the ore processing and ore handling.

The PCA for TSP identifies five components with 90.52% of the data variance as shown in Table 5.5. The first component has factor loadings of Fe, Ni, Cr, K, Pb, Si, Al, SO_4^{2-}, TOC and TC, and it explained 35.79% of the variance. This factor is mainly associated with steel production (Tsai et al. 2007) and cement factory emissions (Lioy et al. 2009) in general. So component one (PC 1) is related to steel production and other industrial activities. The second component explained 22.61% of the total variance having factor loadings of Fe, K, Mg, Si, Al, and TC. These elements are characteristics of soil dust (Callén et al. 2009; Mazzei et al. 2008). The third component explained a total 16.62 % of the data variance and is related to elements like Fe, Zn, K, Pb, Mg, Si and sulphate in anions. Iron, K, Mg, and Si are characteristic elements of road dust(Banerjee et al. 2015). Vehicle brake wear, tyre wear, and oil drip could result in greater abundance in Zn in paved road dust (Watson et al. 2002; Yatkin and Bayram 2008). Zinc is a marker element in addition to Pb for transportation because utilization of Pb as a fuel additive nowadays has been banned (Fang et al. 2004). Total carbon is also the characteristic of vehicular emissions. So third component represents the vehicular pollution and road dust. The fourth component was highly related to sulphate and it explained 11.88% of the total variance. This component was associated with secondary sulphate aerosols (Guo et al. 2009; Pio et al. 1996; Querol et al. 2001; Viana et al. 2008). The fifth component explained 3.64% of the total variance and is related to sulphate, OC, and TC. Diesel exhaust profiles normally are

predominant in sulphates and organic carbon (USEPA). Thus, this component represents the diesel/oil combustion.

Table 5.5. Component weights matrix obtained from TSP samples.

Variables	PC1	PC2	PC3	PC4	PC5
Fe	**0.70**	**0.69**	**0.67**	-0.09	0.51
Ni	**0.61**	-0.31	0.17	0.08	-0.32
Cr	**0.66**	-0.32	0.18	0.09	-0.32
Zn	-0.63	-0.33	**0.78**	0.23	0.32
K	**0.63**	**0.81**	**0.86**	-0.68	-0.32
Cu	0.43	-0.02	-0.12	0.32	-0.23
Pb	**0.68**	0.24	**0.81**	-0.55	0.51
Mg	-0.65	**0.76**	**0.66**	-0.68	-0.31
Si	**0.66**	**0.65**	**0.91**	-0.56	0.83
Al	**0.64**	**0.77**	0.17	-0.16	-0.32
As	-0.66	0.30	0.16	-0.35	0.32
Hg	-0.64	0.31	0.16	-0.69	0.31
Cl-	-0.05	0.57	0.11	-0.84	0.24
PO_4^{3-}	0.05	0.21	0.10	-0.16	-0.17
F^-	0.53	0.32	0.16	-0.59	-0.34
SO_4^{2-}	**0.89**	0.33	-0.35	**0.61**	**0.67**
TOC	**0.75**	0.52	-0.17	-0.10	**0.71**
IC	0.59	-0.32	-0.07	0.11	0.30
TC	**0.64**	**0.62**	**0.73**	0.04	**0.76**
Total Variance %	35.79	22.61	16.62	11.88	3.64

5.2.1 ABSOLUTE PRINCIPAL COMPONENT SCORES (APCS)

The principal component scores and the true zero principal components have been used for the calculation of absolute principal component scores. For each species the measured concentrations have been regressed against calculated APCS. The coefficients of equation represent the estimated concentrations of each species contributed by the sources identified. The time series concentrations of species so generated were then used to estimate the mean concentrations contributed by each of the identified sources of PM_{10} and TSP. These are shown in tables 5.6 and 5.7.

Table 5.6. Source contributions of principal components identified for PM_{10}.

Species	Steel Production		Soil Dust		Road Dust		Oil Combustion		Ore Processing	
	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV
Fe	20.70	21.78	7.92	19.94	10.62	25.08	0.00	7.43	3.31	27.31
Ni	0.04	6.48	0.01	31.91	0.02	2.52	0.01	46.55	1.49	0.83
Cr	0.06	33.33	0.02	2.87	0.03	16.03	0.02	21.06	0.01	36.91
Zn	0.52	12.09	0.20	27.20	0.27	24.14	0.14	15.01	0.08	35.03
K	7.66	48.23	2.93	45.64	3.93	25.70	0.00	1.59	1.22	42.52
Cu	0.02	30.15	0.01	36.11	0.01	1.17	0.00	39.04	0.00	28.81
Pb	0.03	18.55	0.01	41.05	0.02	19.79	0.01	34.85	0.01	12.99
Mg	0.64	41.32	0.24	44.05	0.33	1.92	0.17	47.36	0.10	45.93
Si	0.24	1.56	0.09	11.71	0.12	34.65	0.06	14.25	1.48	1.64
Al	1.12	14.44	0.43	34.43	0.57	22.99	0.29	42.19	0.18	11.18
As	0.00	42.46	0.00	19.85	0.00	46.83	0.00	0.69	0.00	18.46
Hg	0.00	14.10	0.00	12.62	0.00	37.08	0.00	14.09	0.00	13.52
Cl^-	0.57	17.68	0.22	43.95	0.29	42.03	0.15	38.58	0.09	4.13
PO_4^{3-}	0.01	30.60	0.00	37.70	0.00	21.47	0.00	22.35	0.00	31.05
F^-	0.00	1.34	0.00	1.86	0.00	39.48	0.00	21.75	0.00	18.86
SO_4^{2-}	3.74	4.17	1.43	49.86	1.92	19.07	2.41	26.56	0.60	30.10
TOC	9.30	37.55	3.56	17.03	4.77	36.59	5.36	23.24	0.04	45.21
IC	0.03	42.12	0.01	26.97	0.01	25.12	0.00	4.82	0.00	48.60
TC	9.32	25.95	3.57	37.28	4.78	6.82	5.37	6.43	0.04	11.13
Total PM_{10}	53.99		20.67		27.69		13.98		8.66	
% contribution	43.21		16.54		22.16		11.19		6.93	

Based on these mean concentrations computed for PM_{10}, steel production identified as the dominant source contributing 43% of the apportioned mass. Road dust and soil dust accounted for nearly 22% and 17% present respectively and were second and third largest contributors of PM_{10}. The other sources included oil combustion (11%) and ore processing/ ore handling (7%). The percentage source contributions observed for PM_{10} were highlighted in figure 5.3.

Table 5.7. Source contributions of principal components identified for TSP.

Species	Industrial source		Soil Dust		Vehicular Pollution and Road Dust		Secondary Aerosol		Ore Processing	
	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV	Contribution ($\mu g/m^3$)	% STDV
Fe	16.57	52.12	8.64	20.10	5.89	40.37	0.00	19.08	0.72	38.75
Ni	0.03	45.33	0.01	31.72	0.01	56.76	0.01	5.05	0.01	35.20
Cr	0.05	3.61	0.03	52.26	0.02	3.88	0.02	0.06	0.01	22.42
Zn	0.41	23.62	0.21	15.82	0.15	19.53	0.17	50.04	0.10	37.58
K	5.94	13.06	3.10	34.86	2.11	45.34	2.94	10.33	1.40	51.48
Cu	0.03	53.24	0.01	43.13	0.01	43.07	0.01	27.48	0.01	21.77
Pb	0.03	13.01	0.01	14.87	0.15	53.83	0.01	32.80	0.01	47.68
Mg	0.99	17.98	0.52	39.83	0.35	7.94	2.93	11.62	0.23	1.00
Si	0.21	17.58	0.11	3.92	0.07	42.10	0.08	41.78	0.05	54.42
Al	0.89	50.33	0.47	14.06	0.32	27.19	0.36	9.02	0.21	16.56
As	0.00	41.34	0.00	40.21	0.00	4.41	0.00	25.20	0.00	0.53
Hg	0.00	55.14	0.00	32.04	0.00	50.53	0.00	53.99	0.00	20.46
Cl^-	0.41	5.01	0.21	52.20	0.01	20.70	5.23	42.01	0.10	32.05
PO_4^{3-}	0.01	40.62	0.00	25.41	0.00	41.90	1.24	31.36	0.00	36.03
F^-	0.00	52.18	0.00	25.35	0.00	47.55	0.00	5.02	0.00	21.50
SO_4^{2-}	3.06	56.79	1.60	21.20	1.09	37.38	4.71	29.12	3.90	44.56
TOC	12.92	55.24	6.73	3.56	4.59	55.84	2.17	14.67	3.04	55.49
IC	0.45	18.27	0.23	31.57	0.16	22.05	0.18	51.16	0.10	8.21
TC	13.36	50.81	6.97	9.87	4.75	5.72	2.35	50.63	3.15	50.71
Total TSP	55.37		28.86		19.68		22.41		13.04	
% contribution	39.73		20.71		14.12		16.08		9.36	

Emissions from industrial sources mainly steel plant and cement factory were identified as large contributors of TSP and they accounted for nearly 40%. Re-suspension of soil dust into the atmosphere contributed nearly 21%, followed by secondary aerosol (16%). The other sources included vehicular pollution and road dust (14%) and ore processing (9%). The percentage contributions of these sources to TSP in Rourkela are highlighted in figure 5.4.

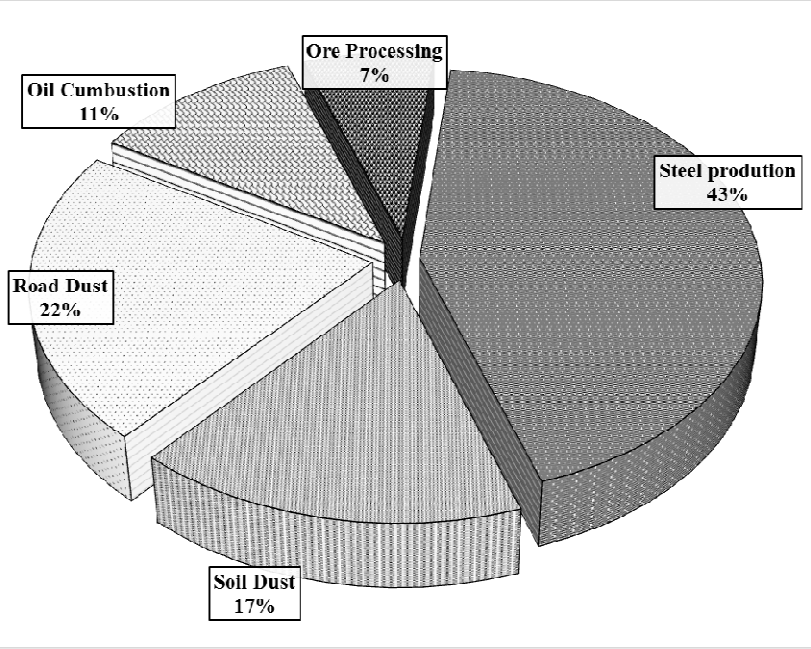

Figure 5.3. Percentage source contributions observed for PM_{10} during the study period.

Correlation analysis between the measured and the predicted concentrations have been performed and were presented in figures 5.5 and 5.6. The correlation coefficient (R^2) values estimated by this analysis were found to be 0.90 for PM_{10} and 0.82 for TSP which is indicative of statistically comprehensive model predictions. The percentage standard deviations have been quantified for each species and it has been observed that the model predictions for most of the species were robust, while some of the species have been slightly frail. In general, the model performance fulfilled most of the qualitative and statistical checks used in source apportionment studies.

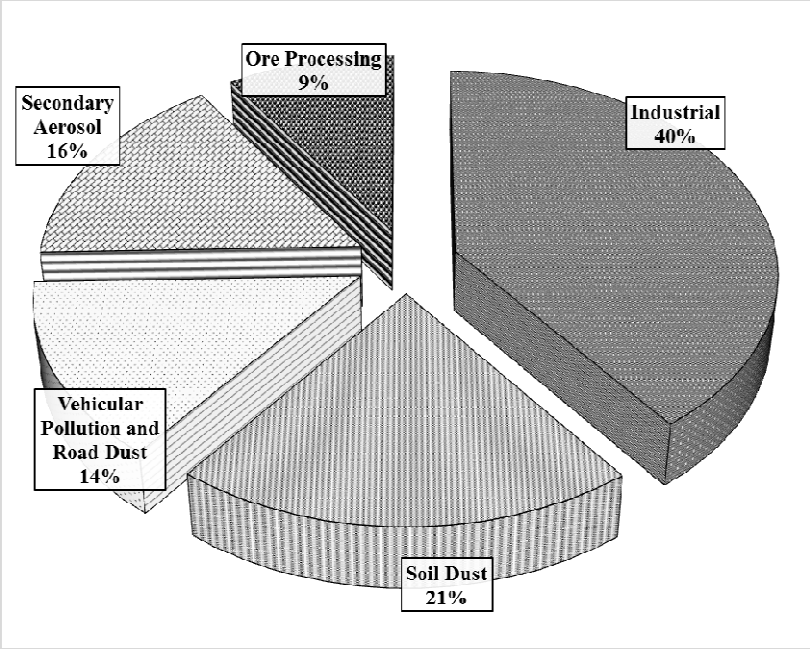

Figure 5.4. Percentage source contributions observed for TSP during the study period.

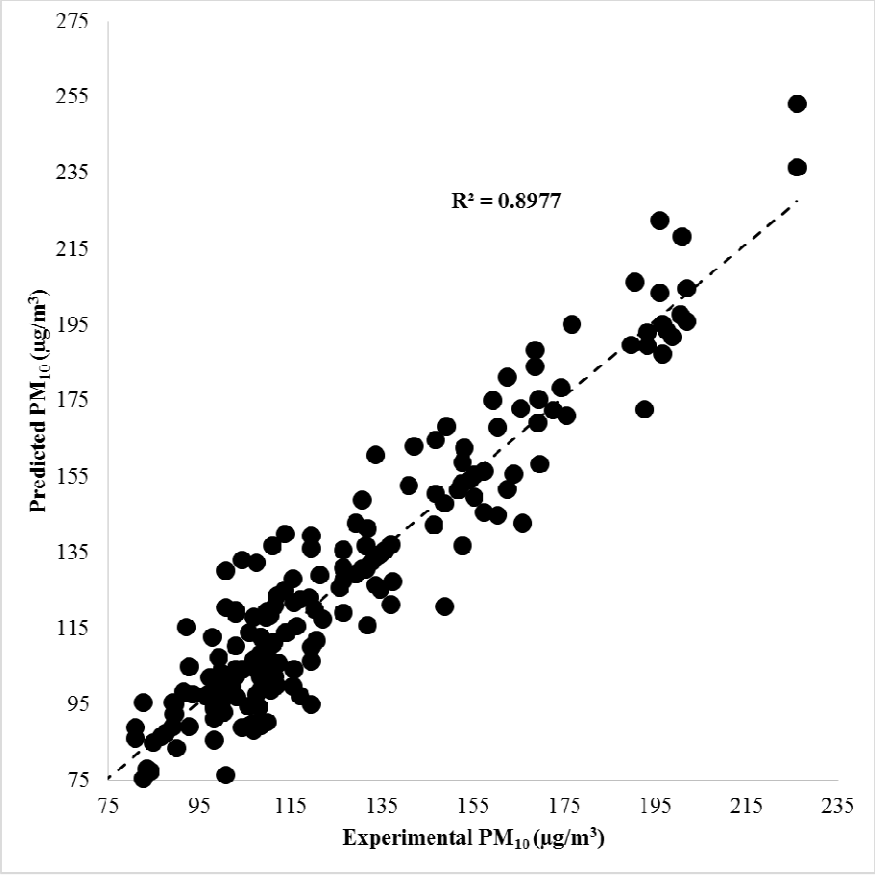

Figure 5.5. Model predicted PM_{10} vs. experimental PM_{10} concentrations.

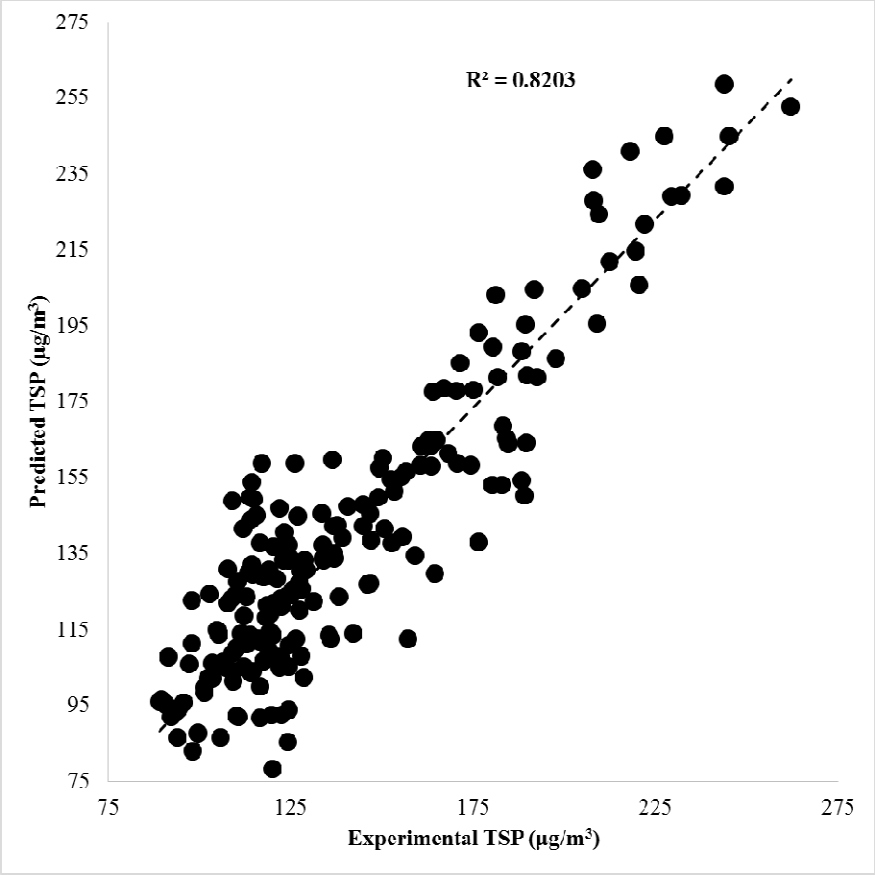

Figure 5.6. Model predicted TSP vs. experimental TSP concentrations.

5.3 POSITIVE MATRIX FACTORIZATION (PMF)

The fundamental philosophy of PMF is to decompose the ambient data matrix. Ambient data(*X)* comprises of concentration measurements of *n* chemical species in *m* samples and their corresponding uncertainties. The PMF decomposes it into two matrices, *G*, the contribution matrix and *F*, the factor profile matrix which can be interpreted by the researcher to *p* number of factors. To model the source receptor concentrations, the US EPA PMF version 5.0 was used. PMF is a multivariate factor analysis technique that has been widely applied in many studies in the recent years. The contribution matrix *G* represents the contribution of each factor to each of the ambient sample and also describes the time variations of the factors. The factor profile matrix

F contains the chemical composition of profile of each factor. PMF calculates the site specific source profiles with time variations of these sources based on the correlations in the ambient data as represented in equation 5.6.

$$X_{(n\times m)} = G_{(n\times p)}F_{(p\times m)} + E_{(n\times m)} \tag{5.6}$$

Where, E is the residual matrix of random errors e_{ij}, for species j measured on sample i.

Thus PMF identifies a set of p factors that best characterize the PM at the receptor. Results are constrained so that no sample can have a negative source contribution, i.e., both the G and F matrix are forced to be non-negative. PMF tries to reproduce x_{ij} by minimizing Q by adjusting the values of g_{ik} and f_{kj} for a given p (eq. (5.7)).

$$Q_{\min} = \sum_{i=1}^{n}\sum_{j=1}^{m}\frac{e_{ij}^2}{u_{ij}^2} \tag{5.7}$$

Where, u_{ij} is the uncertainty of the j^{th} species concentration on sample i, n is the number of samples, and m is the number of species.

Data preparation (to arrange the data in the appropriate form for PMF analysis) is at first performed to guarantee that the information fits the model necessities for input. A matrix of uncertainties for every information point must be supplied for the model, or created in the event that the scientific or technical errors are obscure. In the present study the uncertainties are calculated as follows. If the concentration is less than or equal to the mean detection limit (MDL), the uncertainty (u) is calculated using a fixed fraction of the MDL (eq. (5.8)):

$$u = \frac{5}{6}MDL \tag{5.8}$$

If the concentration is greater than the MDL, the calculation is based on error fraction of the concentration and MDL (eq. (5.9)):

$$u = \sqrt{(ErrorFraction \times concentration)^2 + (0.5 \times MDL)^2} \quad (5.9)$$

During the data preparation for PMF model it is to be decided that if a species needs to be excluded or not. The signal-to-noise (S/N) ratios of the species are useful in determining its presence in the model. The species uncertainty is increased if the S/N value is too low, which decreases its influence on the results. Two calculations are performed to determine S/N, where concentrations below uncertainty are determined to have no signal, and for concentrations above uncertainty, the difference between concentration (x_i) and uncertainty (u_i) is used as the signal (eq. (5.10)):

$$\frac{S}{N} = \frac{1}{n}\sum_{i=1}^{n} d_{ij} \quad (5.10)$$

Where:

$$d_{ij} = \left(\frac{x_{ij} - u_{ij}}{u_{ij}}\right) \qquad if\ x_{ij} > u_{ij}$$

$$d_{ij} = 0 \qquad if\ x_{ij} < u_{ij}$$

As a result of this new S/N calculation, the species with concentrations always below their uncertainty will have an S/N of 0. Species with concentrations that are twice the uncertainty value have S/N value of 1. S/N ratios of different species presented for PMF analysis in this study are summarized in table 5.8. Species with S/N ratios greater than 1 are considered to be good species. But it also depends on the model each individual data. One can decide what is the cutoff S/N ratio according to the satisfaction of model parameters like Q values matching to the total number of data points, rotational ambiguity etc. In case of PM_{10}, species with S/N greater than 3 is categorized to be strong species. In case of TSP, species with S/N greater than 4 is categorized as strong species. Both PM_{10} and TSP values were also given in the input data but

were considered to be weak species so that they cannot be included in the modeling process. Negative concentration values don't add to the S/N, and species with a modest bunch of high concentration occasions won't have falsely high S/N. Out of all the methods to determine S/N, the present method may be more useful in environmental data analysis though with the caution that the S/N is merely one of many analyses for screening data.

Table 5.8. S/N ratios and Categories of both PM_{10} & TSP.

Species	Category	S/N	Species	Category	S/N
PM_{10}	Weak	8.96236	TSP	Weak	8.969595
Iron	Strong	8.997889	Iron	Strong	8.998313
Nickel	Strong	8.190658	Nickel	Strong	8.321158
Chromium	Strong	8.550823	Chromium	Strong	8.62482
Zinc	Strong	8.885774	Zinc	Strong	8.907012
Potassium	Strong	8.997932	Potassium	Strong	8.998259
Copper	Strong	4.203663	Copper	Strong	5.831049
Lead	Strong	7.586768	Lead	Strong	8.000609
Magnesium	Strong	8.969029	Magnesium	Strong	8.992787
Silicon	Strong	8.478457	Silicon	Strong	8.658551
Aluminum	Strong	8.99215	Aluminum	Strong	8.993665
Fluoride	Strong	5.630692	Arsenic	Weak	3.313953
Sulfate	Strong	8.996656	Mercury	Weak	1.828376
Arsenic	Weak	2.462773	Chloride	Strong	8.869338
Mercury	Weak	1.828376	Phosphate	Strong	6.982678
Chloride	Strong	8.868147	Fluoride	Strong	6.093895
Phosphate	Strong	5.671964	Sulfate	Strong	8.997421
Organic Carbon	Strong	8.993843	Organic Carbon	Strong	8.998377
Inorganic Carbon	Weak	1.370319	Inorganic Carbon	Strong	8.748973
Total Carbon	Strong	8.99509	Total Carbon	Strong	8.998782

Missing or zero values in the measured data is also an important consideration as PMF model requires to have all the values to be presented (Reff et al. 2007). When a large percentage of data is missing from a species, it can be removed or replaced, and then assigned a large uncertainty to down-weight the missing value in the analysis (Lee et al. 1999). Geometric mean is often used to replace the missing data, while the uncertainty is multiplied by 3 so that relative

error estimates for missing values are equal to 300% (Polissar et al. 1998; Reff et al. 2007). Mean substitution gives better source composition and fewer anomalous factors than case wise deletion because substitution preserves the samples and stabilizes the system (Huang et al. 1999).

If the uncertainties specified for each data point are truly reflective of the uncertainties in the data, then *Q* should be approximately equal to the number of data points in the concentration dataset. If the uncertainties correctly characterize the data, and every point is perfectly modeled, the resultant *Q* should be approximately the number of species multiplied by the number of observations, minus the number of factors multiplied by the number of species. In this study, the *Q* was required to be within 50% of the calculated *Q* to ensure a reasonable fit of all observations. In the present study there are 196 samples and 19 species for both PM_{10} and TSP i.e., Q should be approximately equal to 3724. This approach will also help in determining the number of factors optimum for the given ambient data. By examining the value of Q for different number of factors, the number (of factors) at which Q is closer to total number of data points is chosen. In case of PM_{10}, Q (true) is found to be 3226 and Q (robust) is found to be 3179 when the number of factors was chosen to be four. In case of TSP, Q (true) is found to be 3695 and Q (robust) is found to be 3625 when the number of factors was chosen to be five.

Mathematically, a pair of factor matrices (*G* and *F*) that can be transformed to another pair of matrices (*G** and *F**) with the same Q-value is said to be "rotated". Rotating a given solution and evaluating how the rotated results fill the solution space is one approach to reduce the number of solutions. Due to non-negativity constraints in PMF, a pure rotation is only possible if none of the elements of new matrices are less than zero. If no rotation is possible, the solution is unique. Therefore, approximate rotations that allow some increase in Q-value and prevent any elements in solution from becoming negative are useful in PMF. The Fpeak values

were varied from –1.0 to -1.5 and evaluated using the G space plotting approach to explore the rotational space and identify the edges of the data. An Fpeak of -0.5 was found to correspond to good G space plots for both PM_{10} and TSP.

Table 5.9. Fpeak rotational summery of PM_{10} and TSP.

PM_{10}				
Fpeak #	**Strength**	**dQ (Robust)**	**Q (Robust)**	**Q (True)**
1	0.5	135.57	3314.2	3229.9
2	-0.5	63.34	3241.9	3231.0
3	1	576.25	3754.8	3243.7
4	-1	231.63	3410.2	3239.6
5	1.5	1331.51	4510.1	3250.2
TSP				
Fpeak #	**Strength**	**dQ (Robust)**	**Q (Robust)**	**Q (True)**
1	0.5	215.1	3840.4	3701.7
2	-0.5	77.9	3703.2	3696
3	1	898.7	4523.9	3708.2
4	-1	283.4	3908.6	3709.7
5	1.5	2084.2	5709.5	3717.8

The Fpeak run summaries for both PM_{10} and TSP were given in table 5.9. In a pure rotation, the *Q*-value would not change because the rotation is simply a linear transformation of the original solution. However, because of the non-negativity constraints of PMF, pure rotations are not usually possible and the rotations induced by Fpeak are approximate rotations, which change the *Q*-value. In general, an increase of the *Q*-value due to the Fpeak rotation with a *dQ* of less than 5% of the Base Run *Q* value is acceptable. From the table 5.9 it is clear that for Fpeak strength of -0.5, the *dQ* values are very less and in acceptable rage.

5.3.1 FACTOR CONTRIBUTIONS AND IDENTIFICATION

Figure 5.7 represents the PMF source profiles for PM_{10}. Figure 5.8 represents PMF factor fingerprints of PM_{10} and Figure 5.9 represents the PMF factor contributions for PM_{10}.

Concentration wise Factor 1 was loaded with Fe, OC, TC, K, SO_4^{2-}, Cl^-, Al, Zn and presence of Pb and Cu in notable proportions and with 10.1 % contribution to the PM_{10}. The combination of Fe with organic carbon and total carbon indicates that it can be due to re-suspended road dust (Gupta et al., 2007). Traffic source profiles generally consists of Cu (due to break lining), Zn (due to tyre wear) and Pb (as a fuel additive) which in turn represents the traffic (Banerjee et al. 2015). Sulfate, chloride, aluminum and potassium are also related to road dust by some of the previous SA studies (Chelani et al., 2008; Gupta et al., 2007). The factor fingerprints also depicts the same when observed that factor 1 represents almost 50% of Pb and 70% Hg (only in minute concentration) and 40% of the Cu that can be majorly be found in suspended vehicular dust. Factor 2 contributes about 40.3% of total PM_{10} and is heavily loaded with Fe, OC, TC, K, Al, Mg, Zn and Cl^-. Although it is loaded with similar species as factor 1 except Mg, a clear picture comes when its fingerprints are observed. It is visible from the fingerprints of factor 2 that it contributes to almost 40% to its entire contributing species which include Fe, Ni, Cr, Zn, K, Mg, Al, F^-, SO_4^{2-}, Hg, OC, IC and TC. Most of these species are of crustal origin (Pant and Harrison 2012). There is a fair chance that factor may be representing two or more sources because of the presence of OC and TC in higher amounts. One of the other sources can be refuse or solid waste burning with loadings of Ni, Cr, OC, TC and traces of Pb (Kothai et al. 2011; Kulshrestha et al. 2009; Negi et al. 1967). The small traces of As also supports the fact that factor 2 may represent some sort of combustion process (Kumar et al. 2001). Factor 3 contributes only about 3.7% of the total PM_{10} and is loaded with Fe, K, Cu, Si, SO_4^{2-}, Cl^-, TC and OC. When the factor fingerprints are observed (Figure 5.8) it is clear that factor 3 dose not contribute significantly to any species other than Cu. Its contribution to the overall Cu in PM_{10} is staggeringly high around 75%. This result indicated that there should be

source which releases copper in to the atmosphere but not in high concentrations but it is responsible for most of the copper suspended in PM_{10}. Upon doing some local survey it was found that there an industry located in Udit Nagar (one of the sampling sites), Rourkela which produces and exports copper powder and copper oxide along with master alloying tablets andiron powder. Thus the factor 3 represents metal powder industry. It can also have some contribution of secondary sulfates. Factor 4 contributes around 45.9% of total PM_{10} and is heavily loaded with almost all the species considered in this study except for Cu (0%) and Hg (0%). Considering the factor fingerprints (Figure 5.8) depicts that factor 4 has major contribution of its entire species.

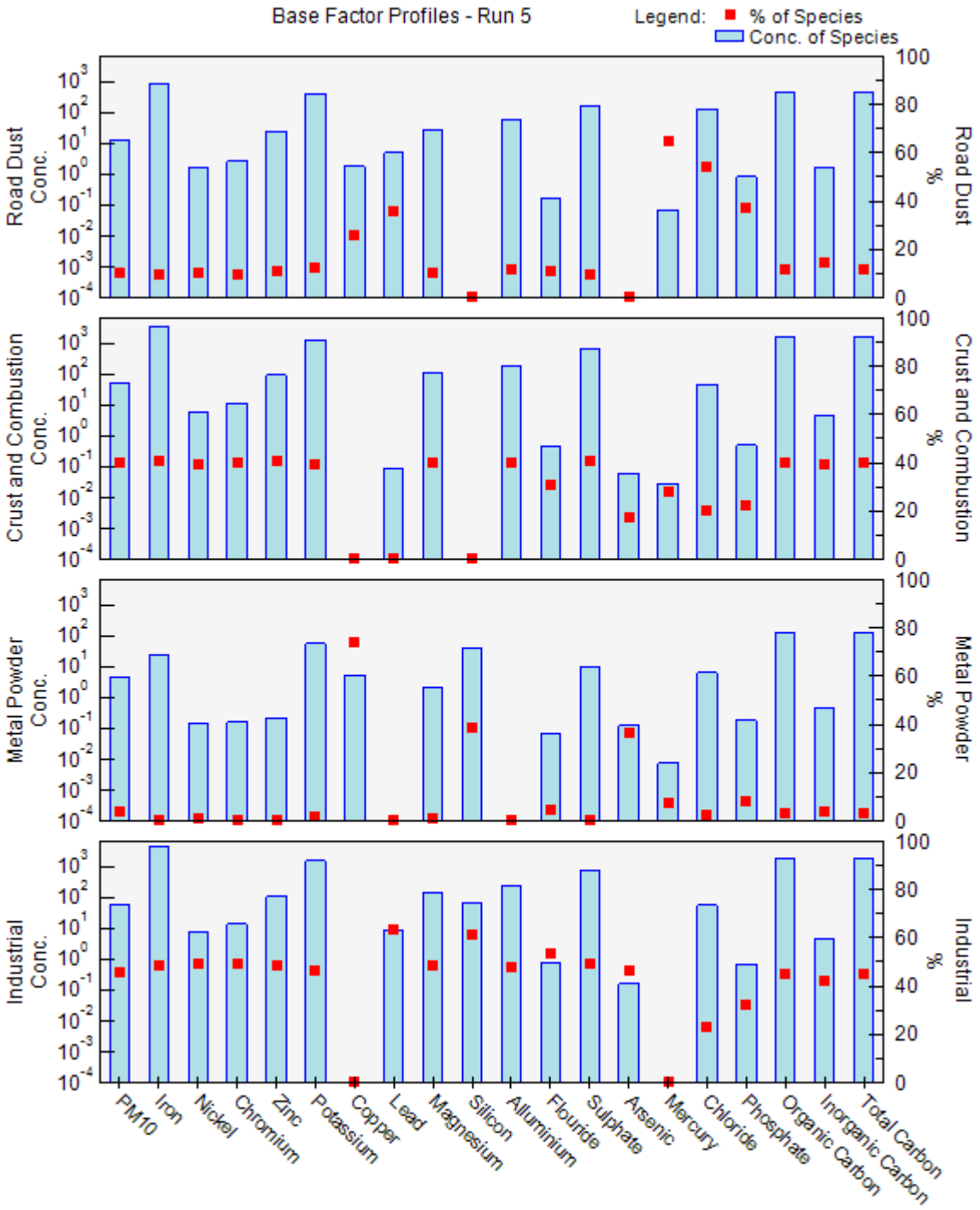

Figure 5.7. PMF source profiles for PM_{10}.

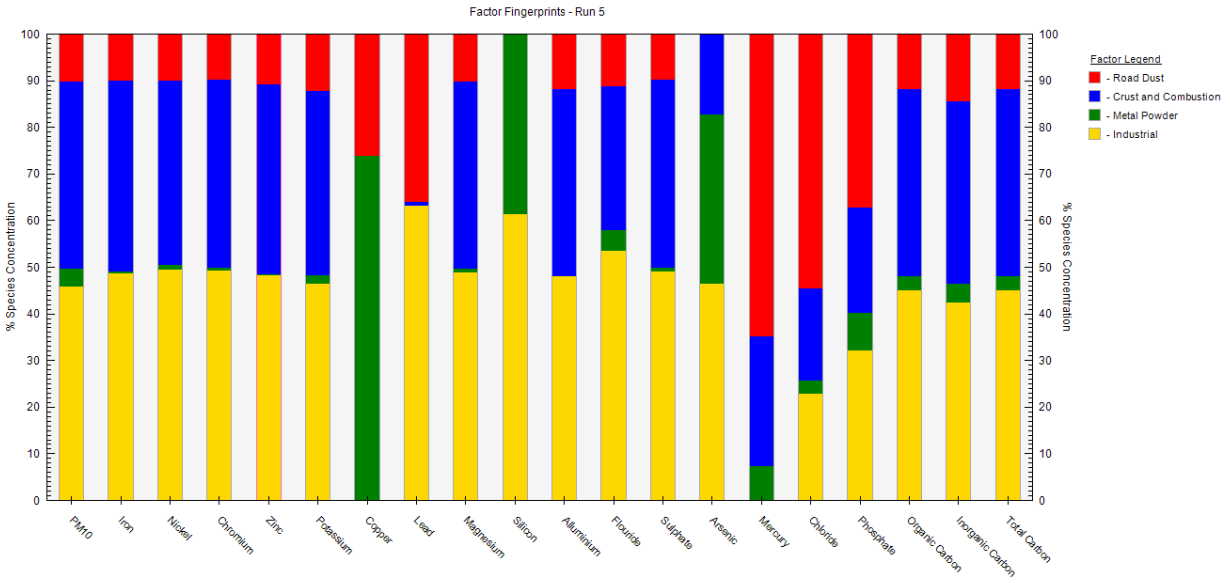

Figure 5.8. PMF factor fingerprints for PM_{10}

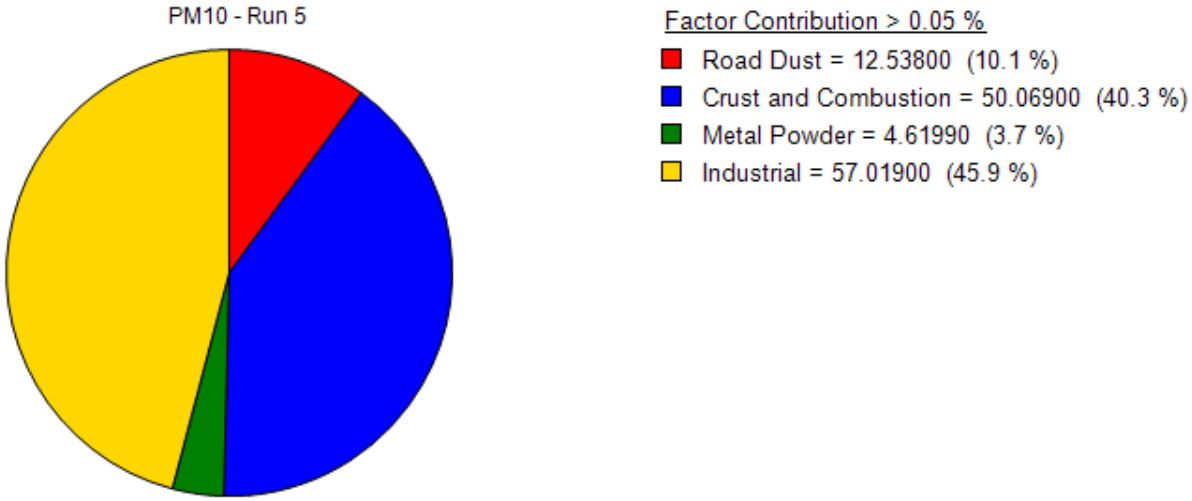

Figure 5.9. PMF factor contributions for PM_{10}.

It clearly represents the industrial sources present in and around Rourkela city. Iron, Ni, Cr, Zn, Pb, Mg, As, and Al are tracer elements of iron and steel industries, smelters, cement factories (Khillare et al. 2004; Kumar et al. 2001; Negi et al. 1967). As most of these productions are based on coal/ coke combustion they release high amounts of SO_4^{2-}, Cl^-, OC, IC, and TC in to the atmosphere (Gupta et al. 2007a; Kumar et al. 2001).

Figure 5.10 represents the PMF source profiles of TSP. Figure 5.11 represents PMF factor fingerprints of TSP and Figure 5.12 represents the PMF factor contributions of TSP.

Factor 1 has a contribution of 25.4% of total TSP and has prominent loading of Fe, K, SO_4^{2-}, Mg, Al, OC and TC. When the factor fingerprints were observed it was found that factor 1 is contributing almost 60% of both As and phosphate. In general biomass combustion and fuel combustion results in contributing As, K, sulfate and phosphate along with OC and TC (Banerjee et al. 2015; Pant and Harrison 2012). Thus factor 1 represents biomass and fuel burning. The contribution of factor 2 to the total TSP is around 23.7% and it is loaded with Fe, K, Zn, OC, TC, Mg and Si. When the factor fingerprints were observed it was prominent that factor 2 is contributing about 65-70% of both Pb and Si. As discussed earlier Pb is one of the tracer element for traffic emissions. All the other elements along with Si represent suspended road dust (Kothai et al. 2011). From this it can be clearly stated that factor 2 represents road dust.

Factor 3 contributes around 41.6% of the total TSP and is heavily loaded with Fe, OC, TC, K, Mg, Zn, Cl^-, SO_4^{2-}. The factor fingerprints reveal that factor 3 is corresponding to 45-50% of its major species with Cu and Pb having 0% loadings on it. As discussed earlier in case of PM_{10}, this factor represents all the different industrial sources around Rourkela city. Factor 4 has a contributing about 5.8% of TSP and is loaded with species like Fe, K, Zn, Cl^-, SO_4^{2-} and Al. But when factor fingerprints were observed it can be seen that almost 80% of Hg is represented by factor 5. Hg in general is a crustal element. Especially in this case because there were hardy any anthropogenic sources possible for it in Rourkela city. More over the concentration of Hg were also so minute that it has to be from crustal source. So factor 4 represents crustal source. Factor 5 has the exact loading pattern as Factor 4 of PM_{10} and is having a contribution of 3.6% to the total TSP. As discussed earlier it is representing the metal powder industry.

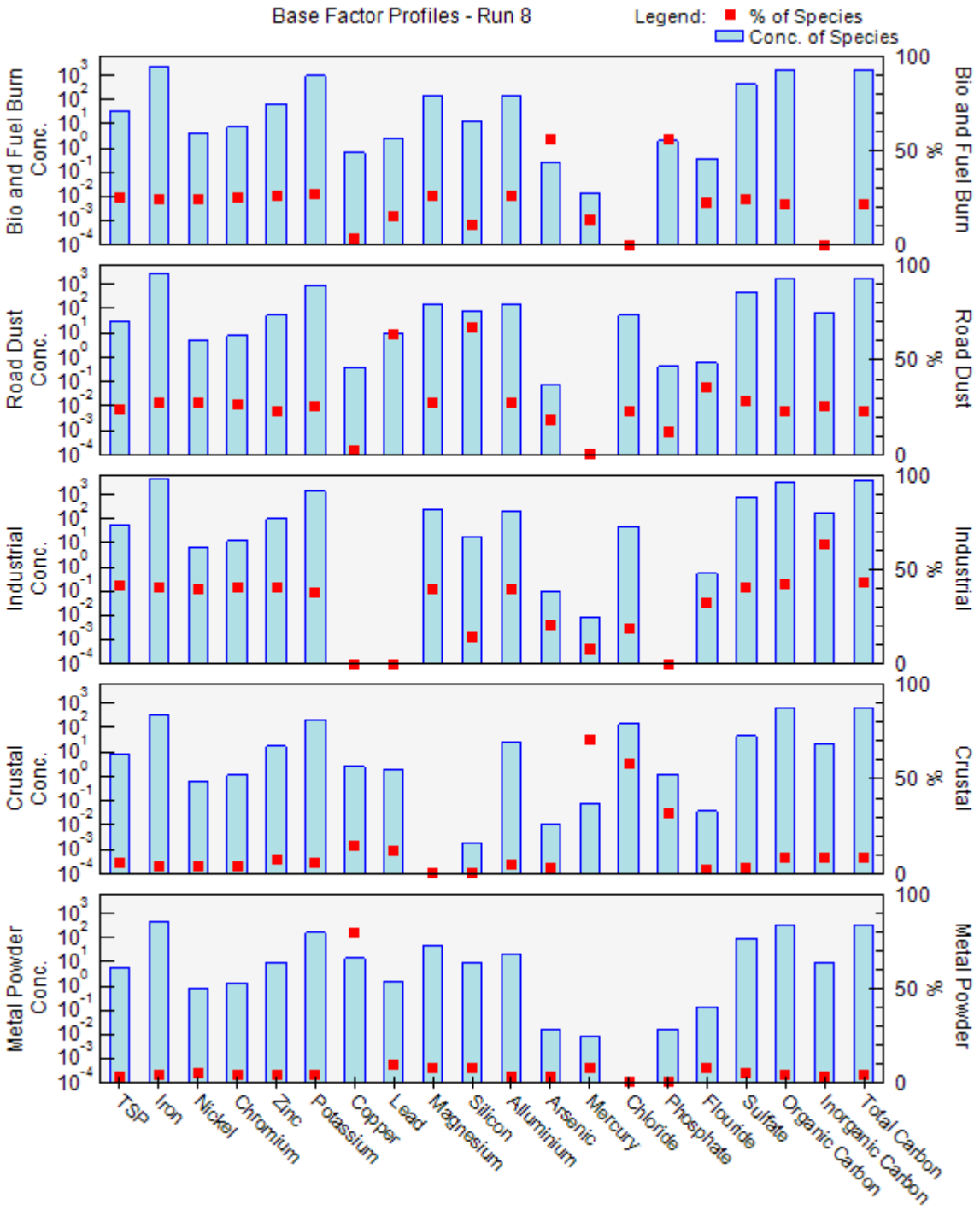

Figure 5.10. PMF source profiles of TSP.

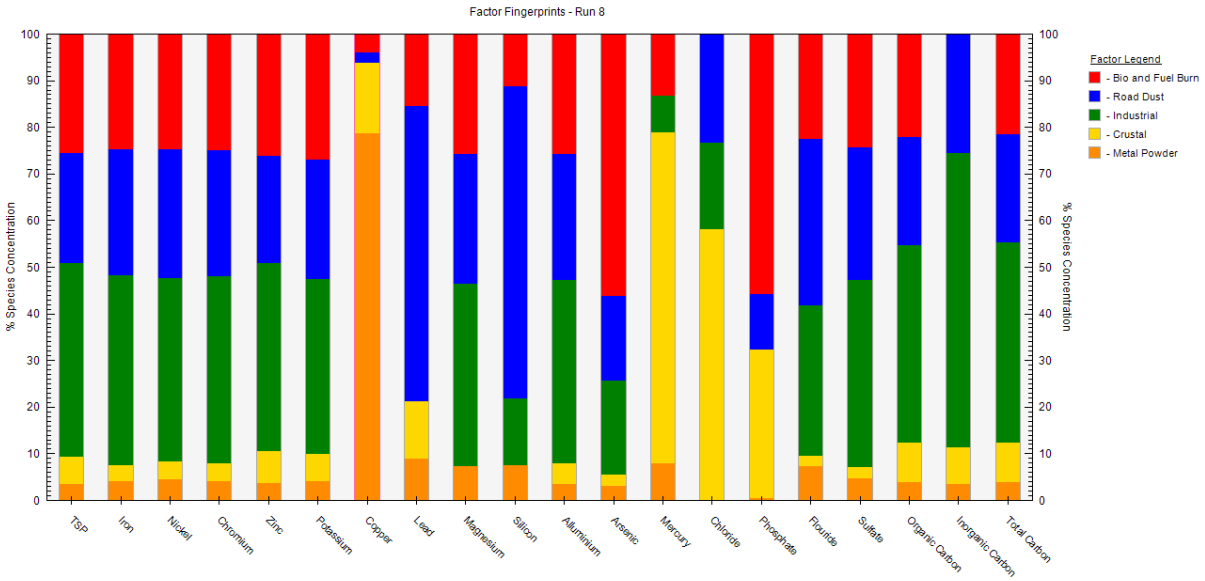

Figure 5.11. PMF factor fingerprints of TSP.

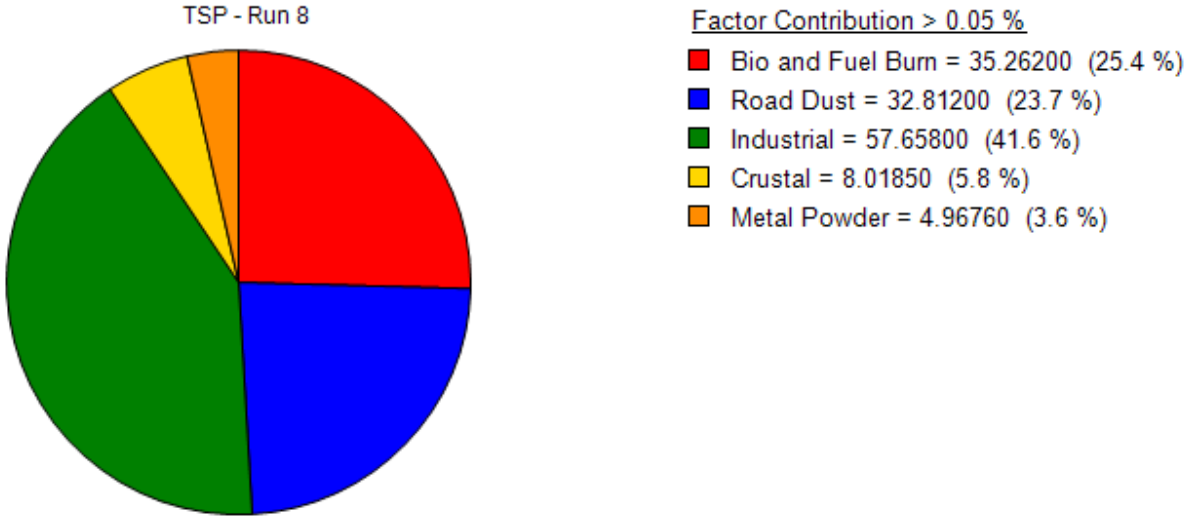

Figure 5.12. PMF factor contributions of TSP.

5.4 COMPARISION OF APPORTIONMENT RESULTS

When compared among the receptor models, CMB, PCA and PMF have shown similar trends in apportioning the PM pollution to different catagories of sources. The sources were sorted into three major groups in this study, namely industrial, crustal and combustion sources.

In case of PM_{10} (Table 5.10), both CMB and PCA have shown very identical contribution of sources, while PMF was unable to distinguish among different source type. This is due to less number of factors chosen for the study.

Table 5.10. Comparision of PM_{10} source apportionment results among receptor models.

Receptor Model	**Industrial (%)**	**Crustal (%)**	**Combustion (%)**
CMB	38.6	28.0	33.4
PCA	43.2	23.5	33.3
PMF	49.6	50.4	

There are different factors that influence the number of factors to be considered for PMF solution. Two of which were 1) By examining the value of Q for different number of factors, the number (of factors) at which Q is closer to total number of data points is chosen. 2) Choosing the number of factors on the basis of interpretability of the factors (source names) based on their loadings. In the present work, the first approach was chosen (section 5.3). This approach has its own limitations that multiple sources may be mapped onto the same factor which did happened in the present study. But choosing the interpretability approach, itresulted in huge deviation of Q values from total number of data points. This means that the uncertainties specified for each data point are not reflecting the uncertainties in the data. If the uncertainties correctly characterize the data, and every point is perfectly modeled, the resultant *Q* should be approximately the number of species multiplied by the number of observations, minus the number of factors multiplied by the number of species.

In case of TSP, all the receptor models have shown similar apportionment results (Table 5.11). All three receptor models have estimated that 40-45% of PM pollution is caused by

industrial sources. They depicted that 30% of PM pollution in Rourkela is from crustal origin. Another 25-30% of PM pollution was apportioned to combustion sources by the receptor models.

Table 5.11. Comparision of TSP source apportionment results among receptor models.

	Industrial (%)	**Crustal (%)**	**Combustion (%)**
CMB	41.6	29.7	28.7
PCA	39.7	30.1	30.2
PMF	45.1	29.5	25.4

CHAPTER 6- AIR QUALITY FORECASTING

6 AIR QUALITY FORECASTING

One of the vital components of present urban air quality management is air quality forecasting. These air quality management systems serve as pioneers for environmental legislation and decision makers in air pollution reduction. The time series records generated by monitoring stations can be used for depicting urban air quality information using methods, tools or human judgment applied over them. Mathematical methods and tools can provide forecasting capabilities, thus offering decision makers with the opportunity to take preventive measures. Recent studies have embraced artificial neural network (ANN) models as an alternative to traditional statistical forecasting methods such as linear regression techniques (Cortina-Januchs et al. 2015). Given the success of ANNs in forecasting and the urgent need for robust forecasts, this chapter explores the efficacy of ANN approaches in forecasting particulate matter (PM) concentrations using meteorological data as inputs. In particular, it tries to compare the performances of multilayer perceptron (MLP) and radial basis function (RBF) algorithms in forecasting using STATISTICA 9.0 software. In so doing, the aim is not to refine predictive models for operational use but to provide a rigorous inter-comparison as a first step toward operational PM forecasting models in Rourkela.

6.1 ARTIFICIAL NEURAL NETWORKS

Artificial neuronal networks (ANN) are powerful data modeling tools with a proven efficiency in dealing with complex problems, particularly in the fields of association, classification and

prediction. Many researchers have shown that neural networks can solve almost any problem more efficiently than the traditional modeling and statistical methods (Hornik et al. 1989; Masters 1993). Typically, a neural network is composed of a set of neurons laid out in layers. Commonly, those layers are classified as input layer, hidden layers and output layer. Some neural networks do not have hidden layers and are used as more linear statistical techniques. These networks (with input and output layers only) are useful in many linear or semi-linear applications, but in general, it is difficult to get accurate results in nonlinear problems (McCullagh and Nelder 1989). It can be recognised that the relation between meteorological data and atmospheric particulate matter is clearly a non-linear problem, at least in the current region of the study. However, there are no specific rules to define how many hidden layers a neural network must have.

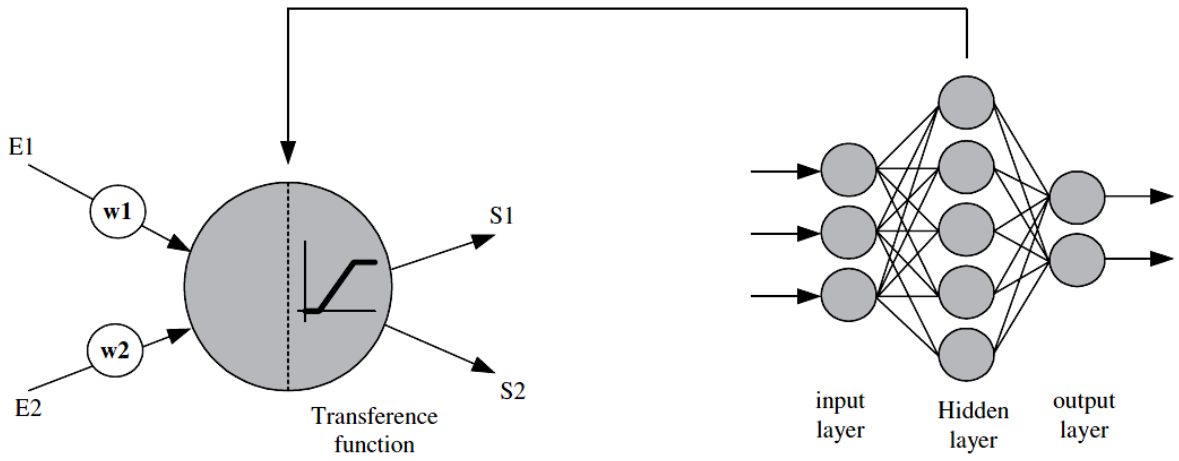

Figure 6.1. A typical artificial neural network structure.

For MLP (multilayer perception) and RBF (radial base function) neural networks, one hidden layer with a large number of neurons usually yield good results (Bishop 1996; Hornik 1993; Hornik et al. 1989). A similar situation occurs in terms of the quantity of data needed to obtain the best training results from the network. The neural network has the capacity to learn

new skills and make predictions from new data, thus it generalizes observed behaviour, rather than simply memorizing a given training data set (Bishop 1996). As a thumb rule, the quantity of data necessary in a neural network analysis would be, for a noise-free quantitative target variable, twice as many training cases as weights, while for a very noisy target variable, 30 times as many training cases as weights may not be enough (Ordieres et al. 2005). The high number of input variables frequently presented in these models implies an even higher number of weights to train if the networks have a fully connected topology thus turning the overwhelming size of the training data set into one of the main obstacles associated with this methodology (Ordieres et al. 2005). Considering these complications of ANN, all the meteorological data and PM data has been refined using moving average filters to make them noise free. Also only four important meteorological parameters have been considered as inputs i.e. temperature, relative humidity (RH), wind speed (WS) and wind direction (WD) to reduce higher number of weights that can tamper with ANN training algorithm. Parameters like precipitation were not considered as they are directly correlated to temperature and RH. Including such parameters will have undesirable effects on training process i.e. overwhelming training data and a bias arising due to correlation between input variables.

6.1.1 MULTILAYER PERCEPTRON (MLP)

Multilayer perception is the most common and successful neural network architecture with feed forward network (FFN) topologies (having three layers of neurons). Each layer uses a linear combination function. The input layers are fully connected to the hidden layer, which is fully connected to the output layers. These networks are used to create a model and map the input to the output using historical data. These networks are called supervised networks. The most common supervised training algorithm is the so called back propagation (Haykin 1998). With

back propagation, the input data are repeatedly presented to the neural network. With each presentation, the output of the neural network is compared to the desired output and an error is computed. This error is then fed back (back propagated) to the neural network and used to adjust the weights such that the error decreases with each iteration and the neural model gets closer and closer to the desired output. This process is known as training. This kind of training is relatively easy and offers good support for prediction applications. It is generally accepted that the characteristics of a correctly designed MLP network are, though worth of comparison, not better than the characteristics that can be obtained from classical statistical techniques. Nevertheless, MLP networks outperform classical statistical techniques in their much shorter time of development, and their adaptive capacity when faced with changes (Ordieres et al. 2005).

6.1.2 RADIAL BASIS FUNCTION (RBF)

The architecture of RBF neural networks is less well known than that of the MLP, although it has been used in time series modeling predictions with good results. The input for this kind of architecture is a feed forward network (i.e., an MLP neuron network), but every unit of the hidden layer has a 'radial basis function' (statistical transformation based on Gaussian distribution function). Like MLP neural networks, RBF networks are suited for applications such as pattern discrimination and classification, interpolation, prediction, forecasting, and process modeling. Unlike MLP networks, the bias term of an RBF neural network connects to the output neurons only. In other words, RBF networks do not have a bias term connecting the inputs to the radial basis units. The 'basis function' (often a Gaussian function) has the parameters 'centre' and 'width'. Usually each unit of the network has a different central value. The centre of the basis function is a vector of numbers C_i of the same size as the inputs to the unit. Normally, there is a different centre for each unit in the neural network.

In the first computation, the 'radial distance' is computed for every unit between the input vector and the centre of the basis function using the Euclidean distance algorithm. In other words, the structure of the RBF has non-linear inputs (input vector) for every data (unit) and the radial distance is computed between the input vector and the centre of the basis function. The input of the RBF neural network is non-linear whereas the output is linear. This means that, unlike an MLP, RBF networks have two types of parameters, (1) the location and radial spread of the basis functions and (2) weights that connect these basis functions to the output units. Figure 6.2 shows the difference between MLP and RBF neural networks in two dimensional input data. While MLP separate the clusters of inputs is to draw appropriate planes separating the various classes from one another, RBF uses an alternative approach to fit each class of input data with a Gaussian basis function(STATISTICA 2015).

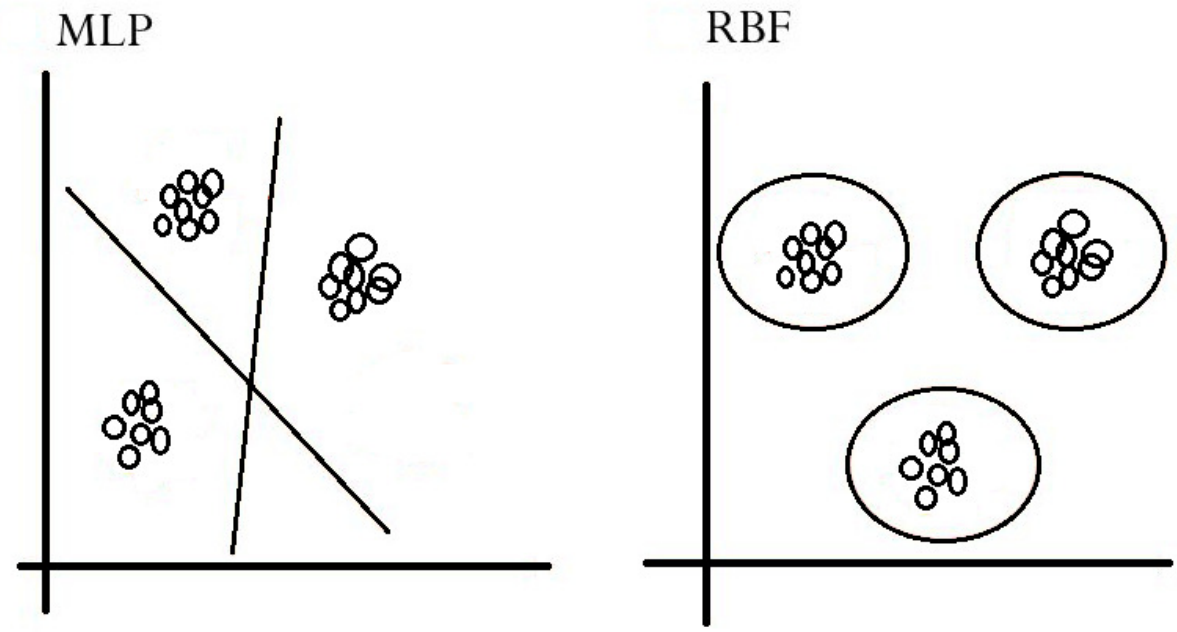

Figure 6.2. Representation of difference between MLP and RBF neural networks in two dimensional input data.

6.1.3 GENERALIZATION AND PERFORMANCE

The performance of neural networks is measured by how well they can predict unseen data (an unseen data set is one that was not used during training). This is known as generalization. The issue of generalization is actually one of the major concerns when training neural networks (Anctil and Lauzon 2004). It is known as tendency to over fit the training data accompanied by the difficulty in predicting new data. While one can always fine tune (over fit) with a sufficiently large and flexible neural network to achieve a perfect fit (i.e., zero training error), the real issue is to construct a network that is capable of predicting on new data as well. As it turns out, there is a relation between overfitting the training data and poor generalization (Figure 6.3). Thus, with training neural networks, one must take the issue of performance and generalization into account. For that purpose the network is repeatedly trained for a number of cycles as long as the test error is on the decreasing trend. When the test error started to increase, training is halted. Note that the number of cycles needed to train a neural network model with test data and early stopping may vary. In theory, one can continue training the network for as many cycles as needed so long as the test error is on the decreasing trend.

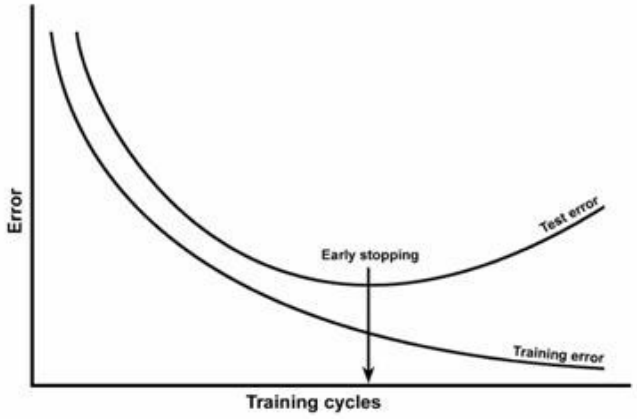

Figure 6.3. Schematic of neural network training with early stopping.

Sometimes, the test data alone may not be sufficient proof of a good generalization ability of a trained neural network. For example, a good performance on the test sample may actually be just a coincidence. To make sure that this is not the case, another set of data known as the validation sample is often used. Just like the test sample, a validation sample is never used for training the neural network. Instead, it is used at the end of training as an extra check on the performance of the model. If the performance of the network was found to be consistently good on both the test and validation samples, then it is reasonable to assume that the network generalizes well on unseen data.

In the present study a total of 186 (from January 2011 to November 2012) samples and their respective meteorological inputs were used for training purpose out of which 15% of data is randomly chosen by the software for testing purpose along with another 15% of the data for validation. The readings of December 2012 (10 samples) have been kept untouched for testing the forecasting capabilities of the neural network that has been trained.

Besides the use of test data for early stopping, another technique frequently used for improving the generalization of neural networks is known as regularization. This method involves adding a term to the error function that generally penalizes (discourages) large weight values. One of the most common choices of regularization is known as *weight decay* (Bishop 1996). Weight decay works by modifying the network's error function to penalize large weights by adding an additional term E_w as explained by equations (6.1 & 6.2)

$$E = E_{SOS} + E_w \tag{6.1}$$

$$E_w = \frac{\sigma}{2} w^T w \tag{6.2}$$

Where σ is the weight decay constant and w is the network weights (biases excluded). Larger the value of σ, the more the weights are penalized. Consequently, too large weight decay

constant may damage network performance by encouraging under fitting, and experimentation is generally needed to determine an appropriate weight decay factor for a particular problem domain. The generalization ability of the network can depend crucially on the decay constant. One approach to choosing the decay constant is to train several networks with different amounts of decay and estimate the generalization error for each; then choose the decay constant that minimizes the estimated generalization error.

This approach will encourage the development of smaller weights, which tends to reduce the problem of overfitting by limiting the ability of the network to form large curvature, thereby potentially improving generalization performance of the network. The result is a network that compromises between performance and weight size. It should be noted that the basic weight decay model described above might not always be the most suitable way of imposing regularization. A fundamental consideration with weight decay is that different weight groups in the network usually require different decay constants. Although this may be problem dependent, it is often the case that a certain group of weights in the network may require different scale values for an effective modeling of the data. Examples of such groups are input-hidden and hidden-output weights. Therefore, in the present work, separate weights decay values were used for regularizing these two groups of weights. The weight decay constants that were used are in the ranges of 0.0001-0.001.

6.1.4 TRAINING ALGORITHM AND ACTIVATION FUNCTIONS

Neural networks are highly nonlinear tools that are usually trained using iterative techniques. The most recommended techniques for training neural networks are the BFGS (Broyden-Fletcher-Goldfarb-Shanno) and Scaled Conjugate Gradient (SCG) algorithms (Bishop 1996). These methods perform significantly better than the more traditional algorithms such as Gradient

Descent but they are, generally speaking, more memory intensive and computationally demanding. Nonetheless, these techniques may require a smaller number of iterations to train a neural network given their fast convergence rate and more intelligent search criterion. STATISTICA Automated Neural Networks provides several options for training MLP neural networks. These include BFGS, Scaled Conjugate, and Gradient Descent. For present study BFGS has shown much better results than the other two, so only MLP networks with BFGS training algorithm were presented here. A multilayer perceptron (MLP) is feedforward neural network architecture with unidirectional full connections between successive layers. However, this does not uniquely determine the property of a network. In addition to network architectures, the neurons of a network have activation functions that transform the incoming signals from the neurons of the previous layer using a mathematical function. Thus, it is important to choose the type of activation function for neurons of a neural network. The input neurons usually have no activation function. In other words, they use the identity function, which means that the input signals are not transformed at all. Instead, they are combined in a weighted sum (weighted by the input-hidden layer weights) and passed on to the neurons in layer above (usually called the hidden layer). The output neuron activation functions are, for most cases, set to the identity but this may vary from task to task. For example, in classification tasks they are set to softmax (Bishop 1996) while for regression problems they are set to identity. The set of neuron activation functions for the hidden and output neurons used in STATISTICA Automatic Neural Networks is given in the table 6.1.

Table 6.1. The set of neuron activation functions for the hidden and output neurons used for both MLP and RBF networks used in STATISTICA Automatic Neural Networks.

Function	**Definition**	**Description**	**Range**
Identity	a	The activation of the neuron is passed on directly as the output	(-∞,∞)
Logistic sigmoid	$\frac{1}{1+e^{-a}}$	An S-shaped curve	(0,1)
Hyperbolic Tangent	$\frac{e^{a}-e^{-a}}{e^{a}+e^{-a}}$	A sigmoid curve similar to the logistic function. Often performs better than the logistic function because of its symmetry. Ideal for multilayer perceptron, particularly the hidden layers	(-1,1)
Exponential	e^{-a}	The negative exponential function	(0,∞)
Softmax	$\frac{\exp(a_i)}{\sum \exp(a_i)}$	Mainly used for (but not restricted to) classification tasks. Useful for constructing neural networks with normalized multiple outputs which makes it particularly suitable for creating neural network classifiers with probabilistic outputs.	[0,1]
Gaussian	$\frac{1}{\sqrt{2\pi\sigma}}\exp\left[\frac{(x-\mu)^2}{2\sigma^2}\right]$	This type of isotropic Gaussian activation function is solely used by the hidden units of an RBF neural network which are also known as radial basis functions. The location (also known as prototype vectors) and spread parameters are equivalent to the input-hidden layer weights of an MLP	

The methods used to train radial basis function networks is fundamentally different from those employed for MLPs. This mainly is due to the nature of the RBF networks with their hidden neurons (basis functions) forming a Gaussian mixture model that estimates the probability density of the input data. For RBF with linear activation functions, the training

process involves two stages. In the first stage, the location and radial spread of the basis functions were fixed using the input data (no targets are considered at this stage). In the second stage, the weights connecting the radial functions were fixed to the output neurons. For identity output activation functions, this second stage of training involves a simple matrix inversion. Thus, it is exact and does not require an iterative process. The linear training, however, holds only when the error function is sum of squares (SOS) and the output activation functions are the identity (STATISTICA 2015). Hence, in the present study, only RBF networks with identity output activation function and SOS error function were presented.

6.1.5 ERROR FUNCTION

The error function is used to evaluate the performance of a neural network during training. It is like an examiner who assesses the performance of a student. The error function measures how close the network predictions are to the targets and, hence, how much weight adjustment should be applied by the training algorithm in each iteration. Thus, the error function is the eyes and ears of the training algorithm as to how well a network performs given its current state of training (and, hence, how much adjustment should be made to the value of its weights). All error functions used for training neural networks must provide some sort of distance measure between the targets and predictions at the location of the inputs. One common approach is to use the sum of squares (SOS) error function as described in equation (6.3). In this case, the network learns a discriminant function. The SOS error is simply given by the sum of differences between the target and prediction outputs defined over the entire training set. Thus, it can be expressed as

$$E_{SOS} = \sum_{i-1}^{N} (y_i - t)^2 \tag{6.3}$$

N is the number of training cases and y_i is the prediction (network outputs) of the target value t_i and target values of the i^{th} data case. It is clear that the bigger the difference between prediction of the network and the targets, the higher the error value, which means more weight adjustments are needed by the training algorithm.

6.2 INPUT VARIABLES

The input variables that have been considered for the modeling of air pollution are presented in table 6.2. The only output variable will be the pollutant concentration. It is interesting to observe the variable corresponding to wind direction index (WDI), considered so as to avoid the discontinuity that it would cause wind direction variable, if used instead. The WDI is defined by the expression as shown in equation (6.4) (Ordieres et al. 2005)

$$WDI = 1 + \sin\left(WD + \frac{\pi}{4}\right) \tag{6.4}$$

Table 6.2. Input variables used and their descriptions for PM predictions.

Variable	**Description**	**Units**
Temperature	Average temperature that has been noted on the sampling day	^{o}C
Wind speed	Average wind speed that has been recorded on the sampling day	m/s
Wind direction index (WDI)	WDI calculated from the equation (22) using the average wind direction noted on the sampling day	-
Relative humidity	Average relative humidity recorded on the sampling day	%

The matrix plot of input variables (temperature, relative humidity, wind speed and wind direction index) and target variables (PM_{10} and TSP) is presented in figure 6.4. Both PM_{10} and TSP have shown a good correlation among themselves and both of them have shown a good

correlation with wind speed. No other significant correlation was found between any other variables.

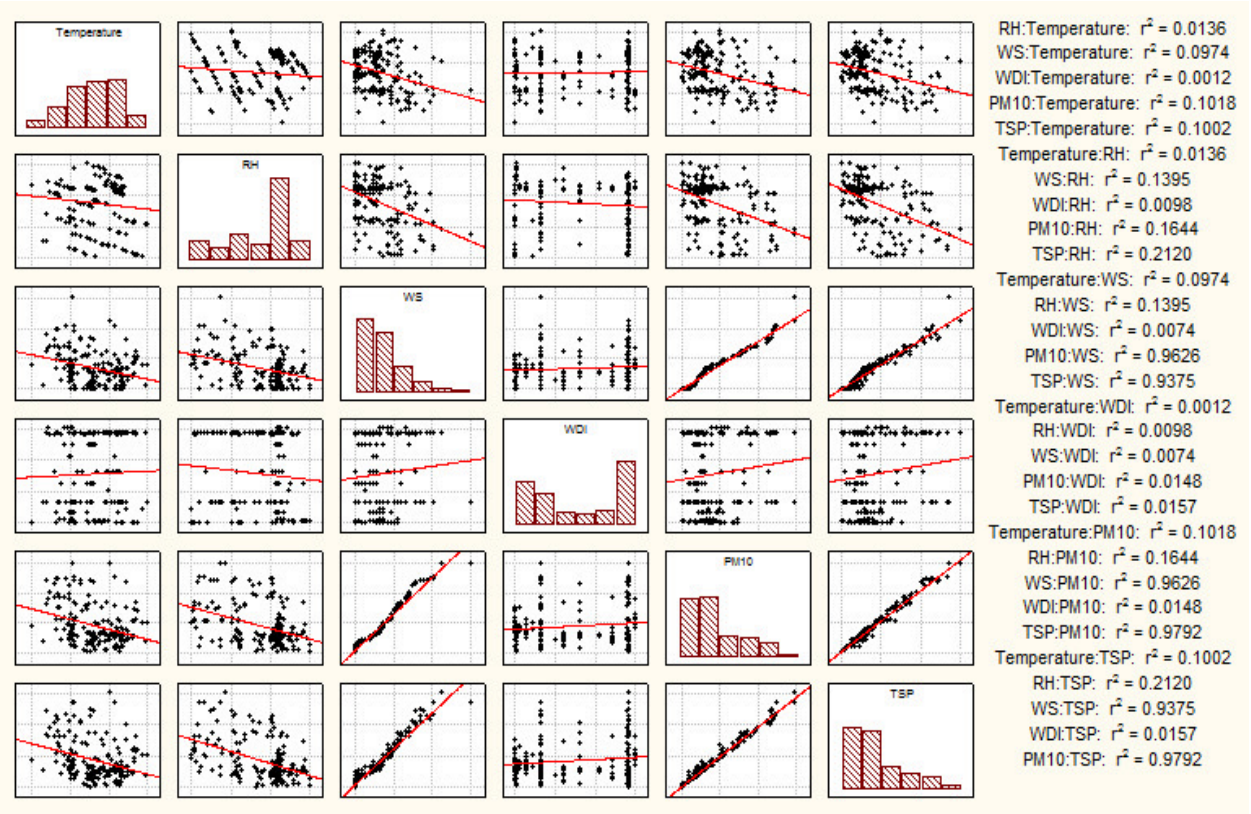

Figure 6.4. Matrix plot of input variables and target variables.

6.3 PREDICTION OF PM_{10} AND TSP USING ANN

The 'statistica automated neural network' (SANN) feature was used to for the prediction of both PM_{10} and TSP using four meteorological parameter (temperature, wind speed, wind direction index and relative humidity) as inputs. A typical neural network is represented in the form of '<name of network> <number of input neurons>- <number of hidden neurons>- <number of output neurons>' (e.g. MLP 4-12-2). The number of input neurons and output neurons are four and two respectively and the number of hidden neurons will be changed for optimized results. SANN feature of STATISTICA 9.0 gives an opportunity to try different combinations of transfer

functions along with a different number of hidden neurons in a given range (1-30 in this case). Out of all the combinations of network architectures, the best 10 combinations were selected and their results were presented in table 6.3. From table 6.3 it is prominent that BFGS algorithm has shown very good prediction capabilities in case of MLP networks. The choice of activation functions has not shown much difference on prediction capabilities of MLP networks as it can be seen all of them were present in top 10 performing networks. In case of RBF networks, the training algorithm will be radial basis function training (RBFT) by default and its hidden activation function will be Gaussian. Identity is found to be the best output activation function in case of RBF network. As discussed earlier, for RBF with linear activation functions, the training process involves two stages. In the first stage, the location and radial spread of the basis functions is fixed using the input data (no targets are considered at this stage). In the second stage, the weights connecting the radial functions to the output neurons are fixed. For identity output activation functions, this second stage of training involves a simple matrix inversion. Thus, it is exact and does not require an iterative process. The same configuration networks that can be seen in top 10 RBF networks (Table 6.3) will vary in the number of epochs that they take in reaching local and global minima during the network training.

Table 6.4 presents the summary of top 10 different combinations of both MLP and RBF networks that have produced best results in predicting the PM_{10} and TSP values by considering meteorological parameters as input variables. From table 6.4, it can be seen that MLP networks have shown some supremacy over RBF networks. The training, testing and validation perfections of MLP networks were better than that of RBF networks. The training, testing and validation errors of MLP networks are significantly lower than that of RBF networks. The training error for regression is calculated from the SOS error defined over the training set. However, the

calculation is performed using the pre-processed targets (scaled from 0 to 1). Similarly, the test and validations error measures are defined as the SOS of the individual errors defined over the test and validation samples, respectively.

Table 6.3. Best 10 configurations of neural networks retrieved for the study.

Net. name	Net. Config	Training algorithm	Hidden activation	Output activation
MLP1	MLP 4-12-2	BFGS	Logistic	Tanh
MLP2	MLP 4-3-2	BFGS	Exponential	Exponential
MLP3	MLP 4-18-2	BFGS	Exponential	Tanh
MLP4	MLP 4-3-2	BFGS	Identity	Logistic
MLP5	MLP 4-14-2	BFGS	Exponential	Logistic
MLP6	MLP 4-3-2	BFGS	Tanh	Logistic
MLP7	MLP 4-8-2	BFGS	Tanh	Exponential
MLP8	MLP 4-12-2	BFGS	Tanh	Logistic
MLP9	MLP 4-5-2	BFGS	Logistic	Tanh
MLP10	MLP 4-3-2	BFGS	Tanh	Identity
RBF1	RBF 4-21-2	RBFT	Gaussian	Identity
RBF2	RBF 4-21-2	RBFT	Gaussian	Identity
RBF3	RBF 4-30-2	RBFT	Gaussian	Identity
RBF4	RBF 4-21-2	RBFT	Gaussian	Identity
RBF5	RBF 4-21-2	RBFT	Gaussian	Identity
RBF6	RBF 4-21-2	RBFT	Gaussian	Identity
RBF7	RBF 4-21-2	RBFT	Gaussian	Identity
RBF8	RBF 4-21-2	RBFT	Gaussian	Identity
RBF9	RBF 4-30-2	RBFT	Gaussian	Identity
RBF10	RBF 4-21-2	RBFT	Gaussian	Identity

Table 6.4. Performances of MLP and RBF networks.

		Training perfection	Test perfection	Validation perfection	Training error	Test error	Validation error
MLP	**Avg**	0.99	0.99	0.99	28.09	27.24	16.58
	Max	0.99	0.99	0.99	33.05	39.28	20.05
	Min	0.99	0.98	0.99	24.58	21.90	14.26
RBF	**Avg**	0.95	0.91	0.94	127.62	232.29	115.98
	Max	0.97	0.95	0.97	189.30	301.48	162.47
	Min	0.92	0.87	0.91	87.66	122.73	60.87

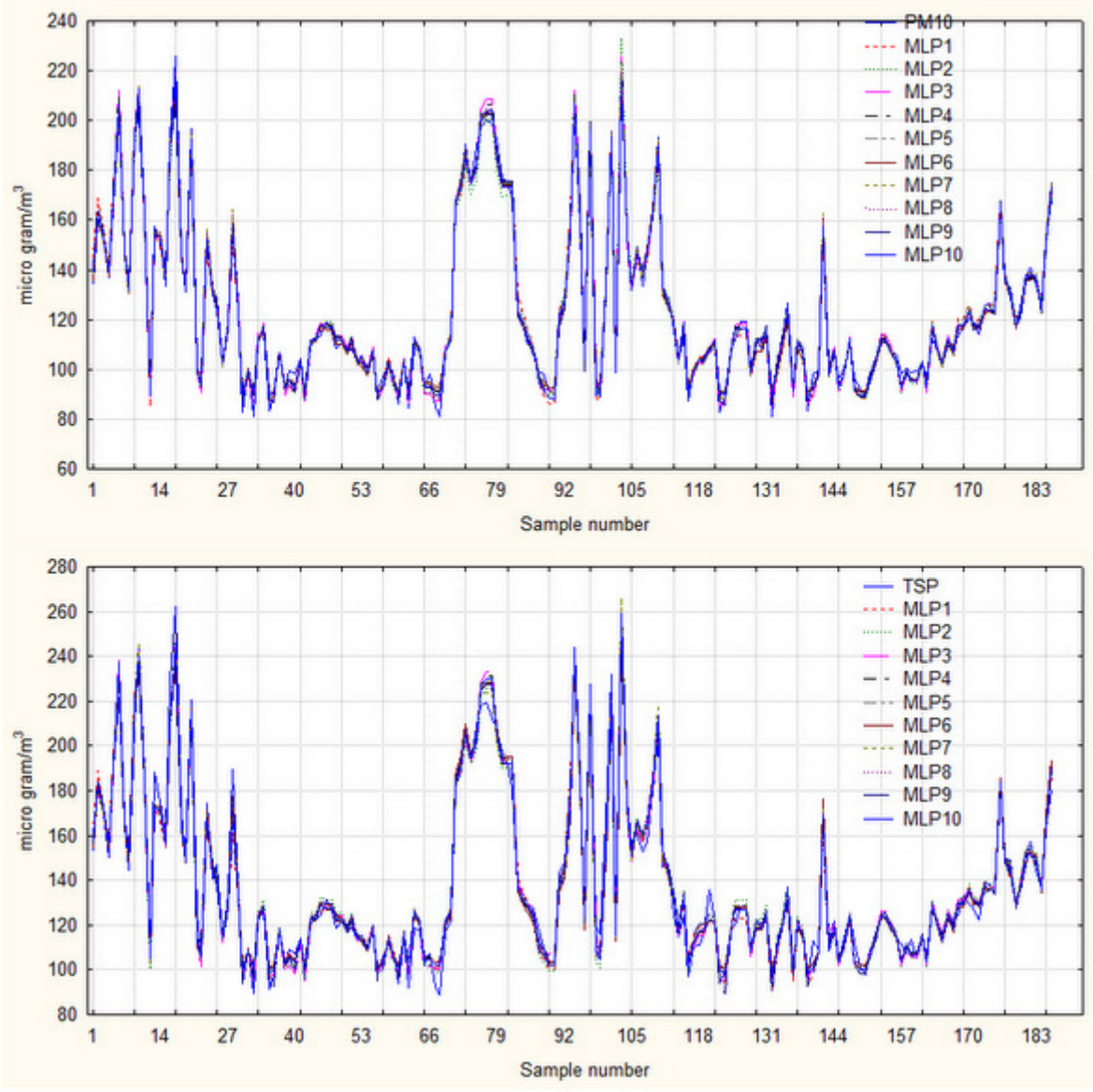

Figure 6.5. Predictions of top 10 MLP networks for both PM_{10} and TSP.

Figures 6.5 and 6.6 show the line plots of measured PM_{10} & TSP and the prediction of 10 different networks of MLP and RBF respectively. Observing the figures will clearly indicate that both MLP and RBF have shown good prediction capabilities while MLP networks were better than that of RBF networks. This slight difference may be coming from the way in which MLP and RBF try to separate the clusters of inputs (Figure 6.2).

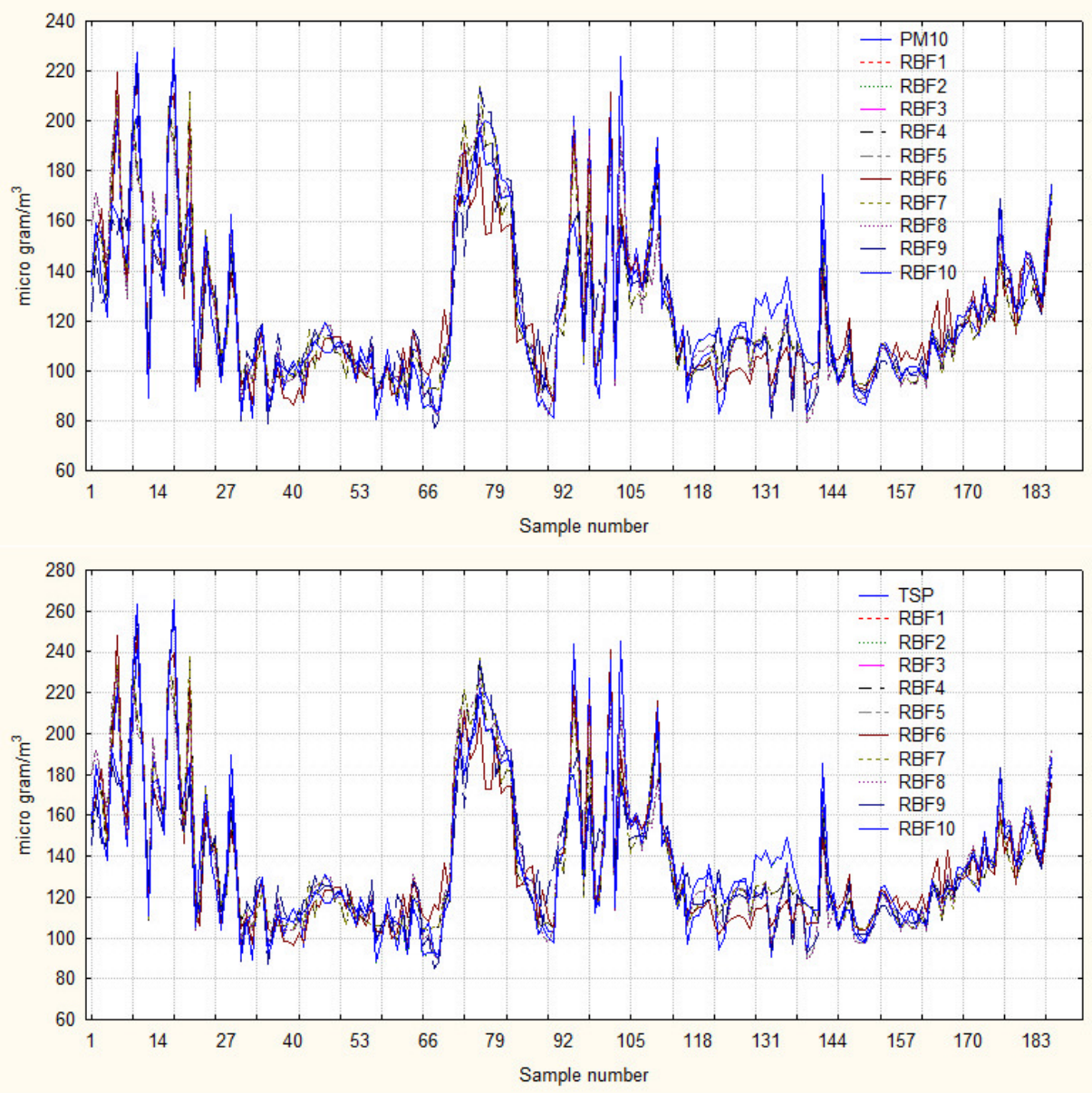

Figure 6.6. Predictions of top 10 RBF networks for both PM_{10} and TSP.

While MLP networks try to separate the input clusters by drawing appropriate planes separating the various classes from one another, the RBF network tries to fit each class of input data with a Gaussian basis function. Thus making it difficult to relate the outliers present in the input data with output data in case of RBF networks (Guo and Luh 2003). Smiler trend was observed in some of the previous related works where MLP networks have shown better air

quality prediction capabilities than RBF networks (Paschalidou et al. 2011; Skrzypski and Jach-szakiel 2008).

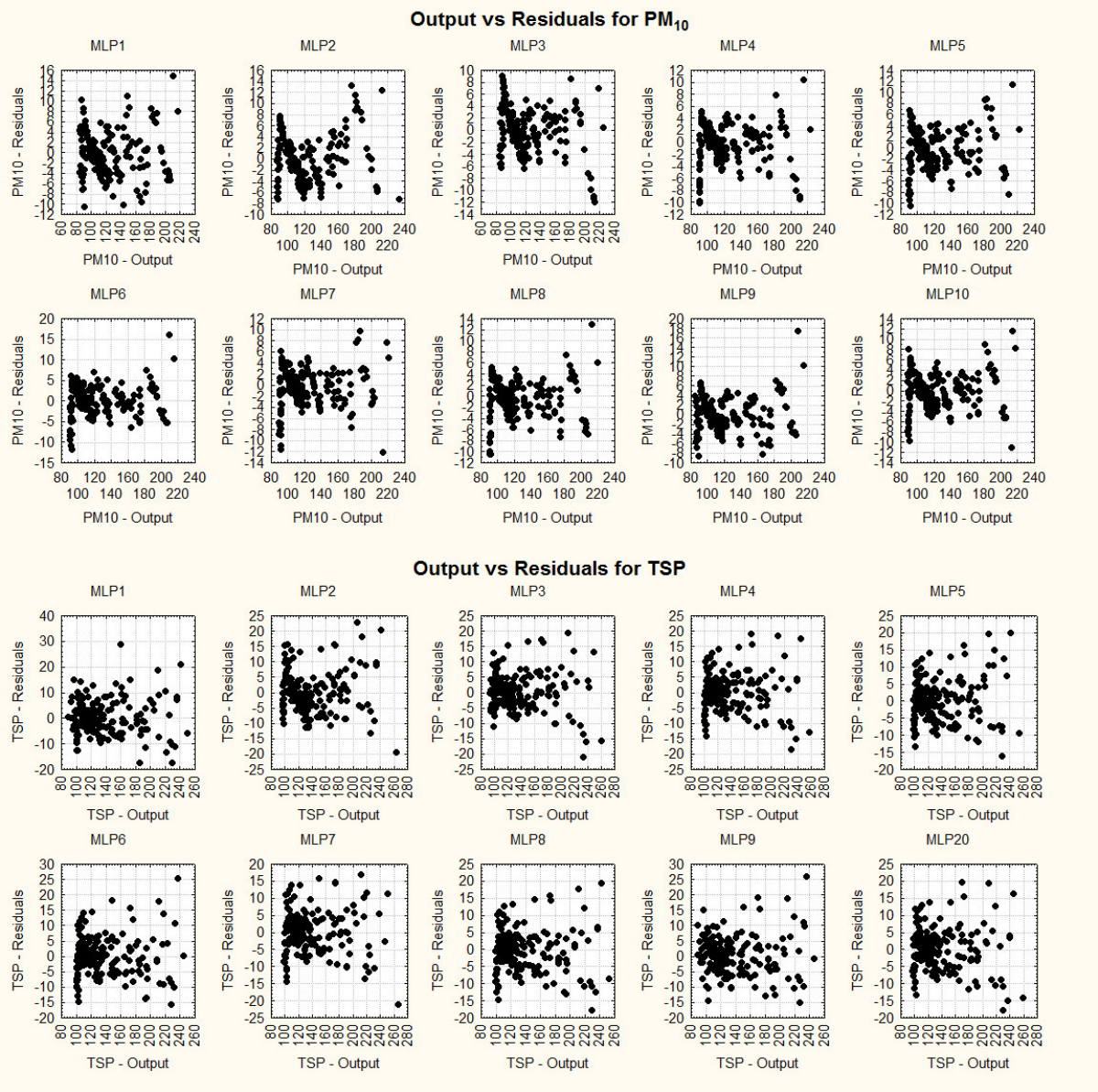

Figure 6.7. Residuals vs. Predicted values of MLP networks for PM_{10} and TSP.

For any statistical or multi-variate regression technique, it is important to check the distribution of errors either around their mean values (histograms) or along with the predicted values. The distribution should not contain any trend being followed by the errors so as to

confirm that the model is not biased at any level or by any other external parameter that was not considered during the modeling process.

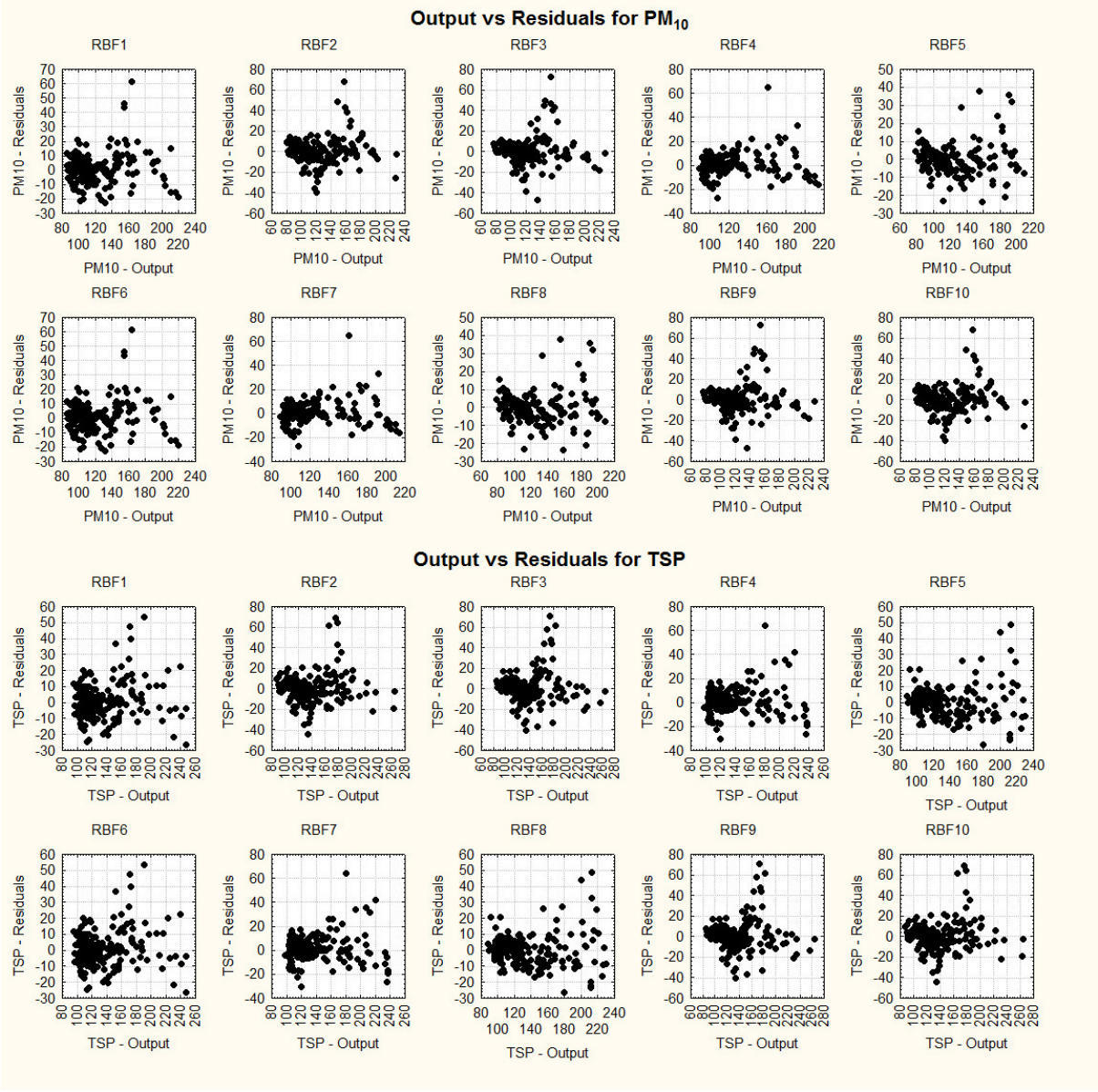

Figure 6.8. Residuals vs. Predicted values of RBF networks for PM_{10} and TSP.

Hence the residuals were plotted against the predicted values of all the networks that were considered. Figures 6 and 7 show the residuals versus predicted values of MLP and RBF networks for PM_{10} & TSP respectively. From the figures, it can be seen that all residuals are randomly distributed, and there is no profound bias that can be seen in the models. Which may

also suggest that there are very few or zero external factors that may influence the dispersion and distribution of particulate matter in the study area.

6.4 FORECASTING OF PM_{10} AND TSP USING ANN

The performances of both MLP and RBF were tested manually by using the data for the month of December 2012 which was kept separately for this purpose. The input variable, i.e., the meteorological parameters of 10 sampling days for the month of December 2012 were fed to the trained ANN and its predicted values were noted. These predicted values were then compared with the original measured values of PM_{10} and TSP for those days. Figure 8 shows the plot for predicted values of PM_{10} & TSP by using MLP networks against the original measured values during December 2012. Figure 6.9 represents the regression between predicted and measure values of PM_{10} and TSP by trained MLP networks while figure 6.10 represents the same by RBF networks.

The thick line in each plot represents the linear fit between measured and predicted values and the dotted lines represent the 95% confidence interval. The r^2 represent the correlation between measured and predicted values, representing the forecasting capacity of the neural network. From the figure 8, it is clearly seen that all the ten MLP networks that were tested had shown good forecasting capabilities with r^2 values ranging between 0.92 and 0.95. In case of TSP also, MLP networks have shown good forecasting capabilities with r^2 values ranging between 0.93 and 0.95. In figure 9 the measured PM_{10} & TSP values for the month of December 2012 are plotted against the predicted values for the same period given by the RBF neural networks. From the figure 9, it is seen that RBF networks lack reliability in predicting the December 2012 values of PM_{10}. Their r^2 values varied from 0.60 to 0.88. In case of TSP also the forecasting capabilities of RBF were not reliable with r^2 values ranging between 0.62 and 0.79.

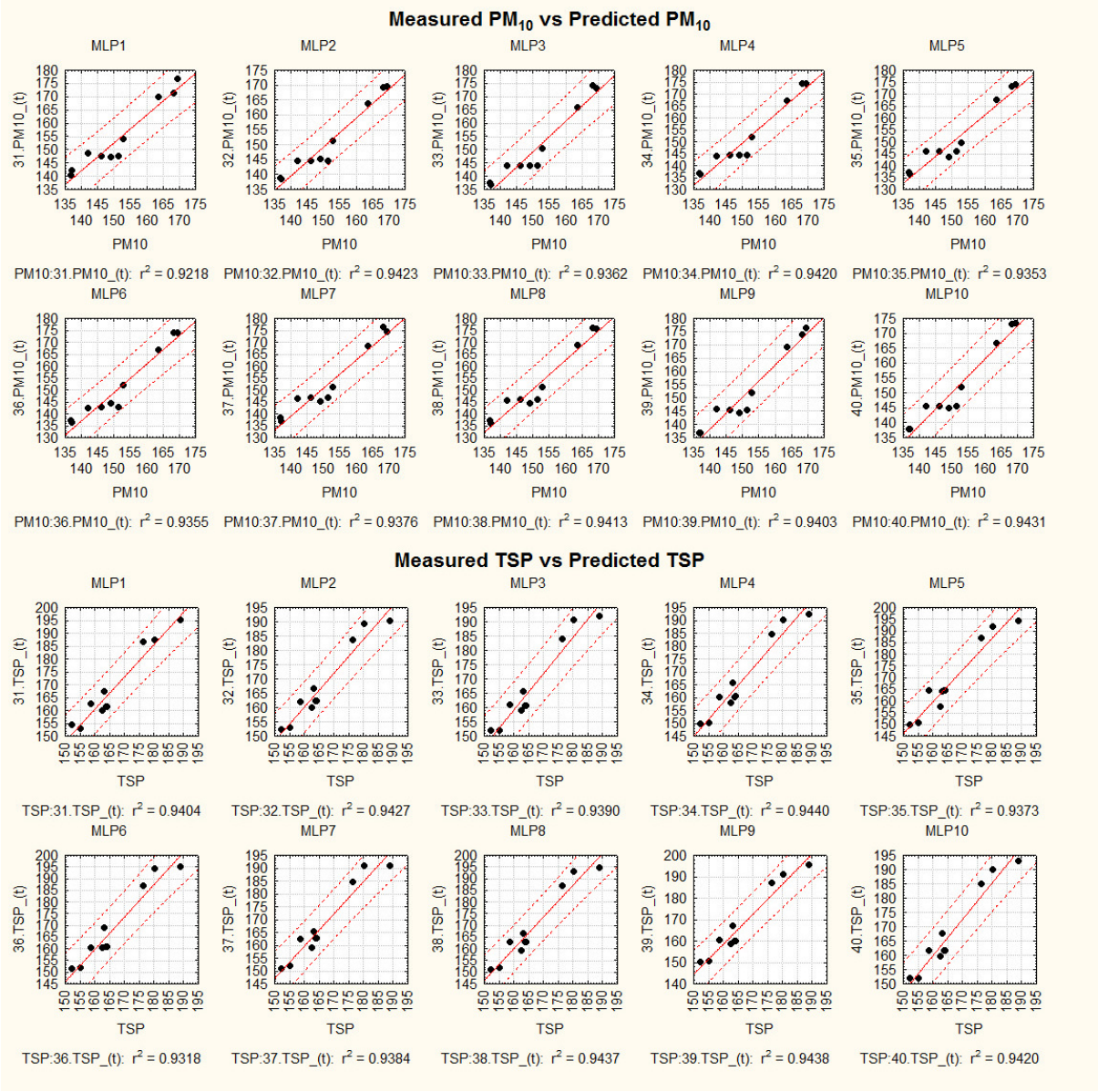

Fig 6.9. Linear regression between predicted and measured values of MLP networks during December 2012

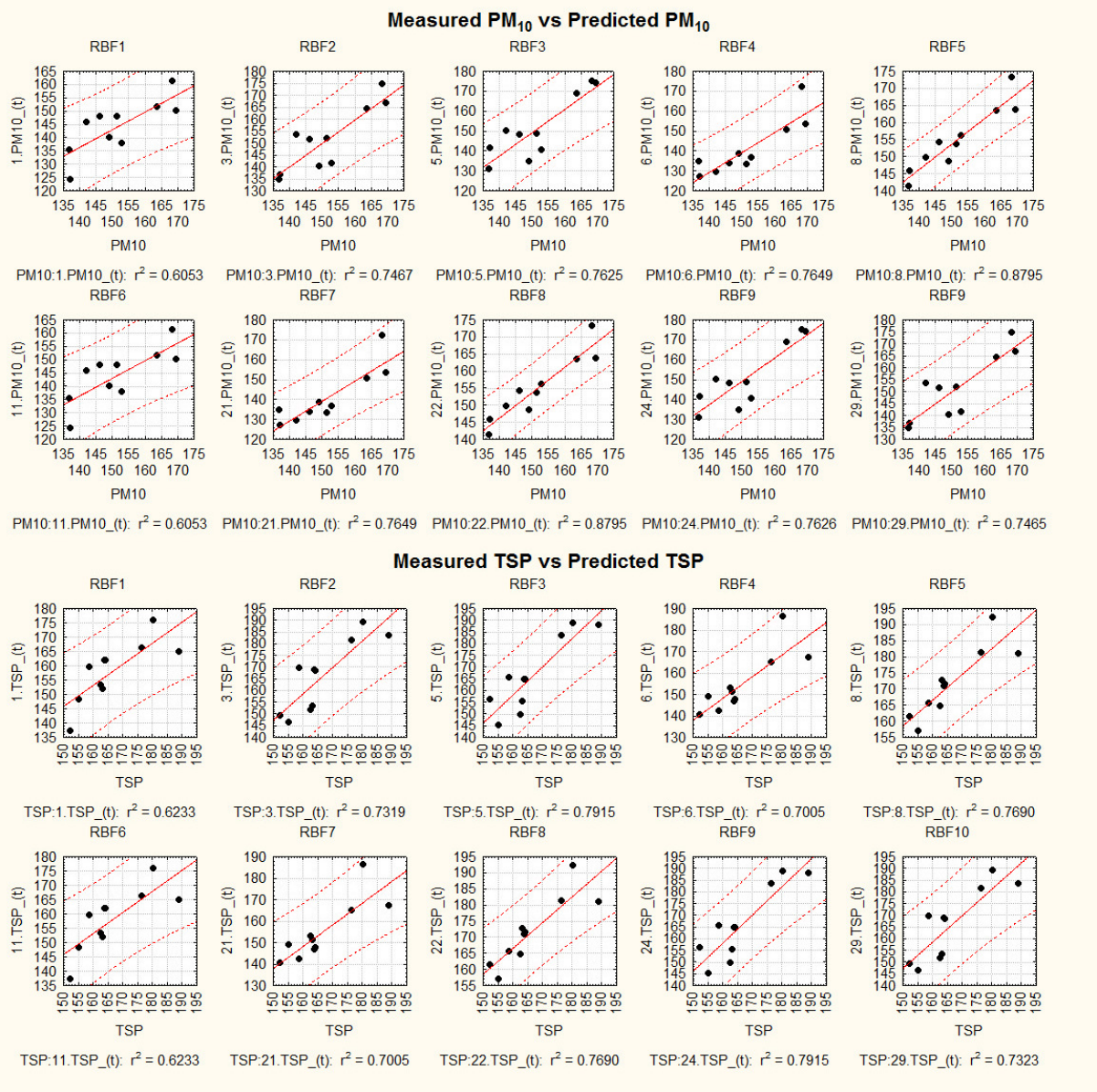

Fig 6.10. Linear regression between predicted and measured values of RBF networks during December 2012

CHAPTER 7- CONCLUSION

7 CONCLUSION

The motive of the present research work is to assert particulate air pollution of a steel city. This work has been the first of its kind to be initiated in India. To fulfil the objectives of present research work, a network of air quality monitoring stations has been selected and particulate matter along with soil and road dust have been studied so that representative sources of particulate air pollution can be determined. The PM_{10}, TSP, soil dust and road dust data along with meteorological parameters such as wind speed, wind direction, rainfall, temperature and relative humidity were measured for 8h duration (9am to 5pm) twice in a week during January 2011 to December 2012. Detailed chemical characterization of PM and dust samples have been performed for their elemental, ionic and carbonaceous species. The conclusions obtained are summarized as

- The seasonal variation of PM observed that all the chemical constituents of particulate matter have followed a trend i.e., summer > spring > winter > monsoon.
- Spearman rank correlation analysis between PM_{10} and its chemical constituents helped in identifying the elements with common sources and different sources that further helped in sources apportionment process.
- Correlation analysis between TSP and its chemical constituents has given an idea about the crustal origins of TSP.

- The enrichment factor analysis highlighted the anthropogenic sources of particulate pollution.
- Receptor models with known source profiles (CMB) and unknown source profiles (PCA and PMF) were used for the sources apportionment.
- Most of the source profiles used for CMB analysis were obtained from CPCB, India. The soil dust and road dust profiles were prepared in the present work particularly for steel city, Rourkela. These two profiles can be used for most of the steel cities present in India.
- Receptor models with unknown source profiles i.e., both PCA and PMF have identified almost similar types of sources, except the PMF model that identified a unique profile which represented a metal powder industry.
- All three receptor models have given comparable results depicting that industrial and combustion sources caused 60%–70% of particulate pollution in Rourkela.
- Empirical modeling has been done using the meteorological and air quality data to produce a model that can interpret the pollutant concentrations at a given point of time for steel city, Rourkela.
- Both PM_{10} and TSP have shown a good correlation within themselves and both of them have shown a good correlation with wind speed. The training, testing and validation perfections of MLP networks are better than that of RBF networks.
- The MLP neural networks have predicted both PM_{10} and TSP values to the perfection whereas there is an error still remaining in prediction of RBF networks. The performances of both MLP and RBF have been tested manually by using the December 2012 data.

- The MLP networks that have been tested shown good forecasting capabilities in case of PM_{10} and TSP with regression coefficients between original and predicted values ranging between 0.92-0.95 and 0.93-0.95, respectively.
- The RBF networks were not that much consistent in predicting the December 2012 values of PM_{10} and TSP with regression coefficients between original and predicted values ranging between 0.60-0.88 and 0.62-0.79.
- In conclusion, the present study tried addresses an important aspect of the urban air quality management programme (UAQMP) in Rourkela steel city i.e. modeling of PM pollution. The source apportionment studies have highlighted the prominent soucres that contribute to the ambient particulate air pollution in the city. This will help in designing control measures to reduce the PM pollution in Rourkela city. The forecasting models have shown their capabilities in predicting the PM pollution in near future. This will help in designing preventive measures in advance for the control of PM pollution in Rourkela city.

7.1 SCOPE FOR THE FUTURE WORK

- In the present research, the sampling at different locations was done consecutively with single sampler. Using multiple samples at a time and simultaneously sampling at different locations will help in further analysis of spatial variations. This will further help in identifying the impact of each source at each location.
- In the present study, the sampling was done during working hours of the day (9 am to 5 pm). Taking 24 hours sample readings will further expand our understanding of particulate pollution in Rourkela steel city.

- In forecasting, only the meteorological parameters were used in predicting the PM concentrations. Including other factors like traffic count and daily steel production will further improve the prediction capabilities of ANN.
- Source dispersion modeling for elevated emission, road dust etc can be carried out, which will be complementary to receptor modeling leading to a comprehensive source apportionment study.

CHAPTER 8- REFERENCES

8 REFERENCES

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APPENDIX I

QA/QC results of PM_{10} and TSP (in $\mu g/m^3$).

Date	PM_{10}			TSP		
	x1	x2	x3	x1	x2	x3
Thursday, January 20, 2011	136.96	130.46	137.16	154.43	144.63	152.43
Sunday, January 23, 2011	162.81	155.81	156.31	191.61	179.71	178.81
Sunday, January 30, 2011	161.87	149.07	154.87	171.97	166.47	174.97
Sunday, February 20, 2011	145.78	131.38	134.68	151.56	145.96	152.86
Wednesday, February 23, 2011	171.92	164.42	171.02	194.97	186.07	187.87
Sunday, February 27, 2011	202.18	198.88	203.08	225.13	213.03	223.03
Friday, March 04, 2011	158.75	146.25	146.05	169.13	159.53	164.43
Friday, March 18, 2011	134.06	129.76	136.76	153.48	141.68	147.08
Saturday, March 19, 2011	197.03	186.43	199.63	212.50	207.60	206.30
Wednesday, March 23, 2011	210.22	196.62	198.02	249.93	235.93	240.73
Saturday, March 26, 2011	172.30	159.40	163.10	191.74	179.14	188.84
Thursday, March 31, 2011	97.32	84.22	92.32	115.98	102.28	112.58
Tuesday, April 05, 2011	167.21	148.91	153.41	193.15	182.65	193.65
Saturday, April 09, 2011	156.25	147.75	154.45	179.18	166.28	176.08
Saturday, April 16, 2011	137.06	130.06	140.56	170.23	157.63	156.43
Monday, April 18, 2011	201.66	191.56	193.26	231.46	220.56	229.26
Thursday, April 21, 2011	229.33	223.13	227.33	267.04	257.64	268.84
Saturday, April 23, 2011	156.16	139.36	142.66	175.51	161.61	165.51
Thursday, April 28, 2011	139.38	122.58	128.78	157.43	147.73	151.03
Saturday, April 30, 2011	200.33	193.33	201.53	223.04	218.84	216.04
Monday, May 02, 2011	103.54	92.54	104.64	131.49	114.59	128.69
Sunday, May 08, 2011	104.79	91.89	94.99	113.93	108.13	107.83
Sunday, May 22, 2011	156.15	150.15	157.65	179.29	172.09	174.29
Friday, May 27, 2011	138.64	122.44	134.34	143.94	138.64	142.54
Sunday, May 29, 2011	138.27	127.37	130.67	156.41	140.71	150.11
Thursday, June 02, 2011	111.94	98.54	101.84	123.51	107.91	118.71
Sunday, June 05, 2011	127.16	109.36	121.06	137.77	127.57	134.97
Sunday, June 12, 2011	163.19	158.19	163.99	194.84	182.14	189.44
Thursday, June 16, 2011	129.77	119.07	121.07	143.69	135.69	132.99
Sunday, June 19, 2011	85.40	77.30	88.30	102.55	89.85	94.25
Wednesday, June 22, 2011	103.65	91.65	100.35	116.67	101.87	112.07
Sunday, June 26, 2011	87.28	74.48	81.38	90.74	86.94	88.24
Wednesday, June 29, 2011	118.44	108.44	113.94	128.59	117.99	126.09
Sunday, July 03, 2011	122.44	112.04	109.44	132.22	121.02	125.02
Tuesday, July 05, 2011	88.45	78.65	79.15	94.69	87.29	94.49

Friday, July 08, 2011	96.52	83.22	91.12	102.67	90.67	90.67
Sunday, July 10, 2011	114.63	100.73	104.53	118.64	114.24	123.84
Wednesday, July 13, 2011	93.75	83.85	97.35	107.22	92.02	101.12
Sunday, July 17, 2011	108.77	93.87	99.57	118.75	104.75	112.75
Wednesday, July 20, 2011	102.76	93.26	99.26	115.10	99.50	111.10
Sunday, July 24, 2011	110.22	97.12	101.22	124.16	111.56	116.36
Wednesday, July 27, 2011	96.09	80.79	85.19	100.12	86.32	92.42
Sunday, July 31, 2011	113.73	106.73	114.13	128.97	116.87	112.37
Wednesday, August 03, 2011	117.56	102.06	114.76	128.14	121.14	129.04
Sunday, August 07, 2011	115.66	105.56	111.36	125.49	114.29	119.19
Wednesday, August 10, 2011	125.38	114.48	123.28	139.52	122.62	132.52
Saturday, August 13, 2011	117.09	110.09	123.09	127.93	119.13	127.93
Tuesday, August 16, 2011	116.44	102.94	112.54	125.86	110.46	118.96
Sunday, August 21, 2011	118.37	109.07	118.77	130.59	118.79	120.49
Friday, August 26, 2011	111.49	97.49	105.89	121.18	112.78	122.28
Sunday, August 28, 2011	112.26	105.36	111.86	124.63	109.53	119.23
Friday, September 02, 2011	111.22	101.32	101.52	115.24	102.84	111.34
Sunday, September 04, 2011	114.26	102.96	105.86	121.24	111.44	112.34
Thursday, September 08, 2011	110.19	90.29	104.09	118.56	107.26	110.86
Sunday, September 11, 2011	117.54	103.64	112.14	120.69	108.79	119.49
Wednesday, September 14, 2011	95.16	81.26	88.36	105.93	88.63	102.23
Sunday, September 18, 2011	102.48	88.68	92.88	110.49	104.69	105.99
Thursday, September 22, 2011	109.94	100.54	104.24	120.14	102.54	115.94
Sunday, September 25, 2011	102.66	90.06	100.96	114.67	104.77	109.87
Thursday, September 29, 2011	92.65	82.85	81.25	96.23	92.23	96.33
Wednesday, October 12, 2011	109.82	98.22	108.02	121.76	112.06	117.66
Sunday, October 16, 2011	88.78	74.88	83.78	100.28	89.18	87.28
Friday, October 21, 2011	110.54	105.64	103.34	122.58	114.08	120.38
Sunday, October 23, 2011	108.81	99.91	106.71	118.97	114.27	116.17
Tuesday, October 25, 2011	95.44	83.84	97.64	109.30	100.80	106.50
Sunday, October 30, 2011	107.56	92.36	93.46	114.40	98.70	106.30
Wednesday, November 09, 2011	86.00	76.50	84.90	98.39	90.49	93.89
Sunday, November 13, 2011	90.32	71.22	78.02	91.53	85.43	89.03
Friday, November 18, 2011	114.93	98.53	111.63	122.74	115.44	119.64
Sunday, November 20, 2011	117.94	101.54	114.74	123.59	118.09	126.39
Wednesday, November 23, 2011	172.89	163.59	172.29	188.13	179.03	188.13
Sunday, November 27, 2011	177.35	166.25	172.75	191.72	181.42	182.92
Wednesday, November 30, 2011	195.70	182.20	188.10	213.18	204.08	205.08
Sunday, December 04, 2011	184.14	173.14	180.24	193.78	185.98	184.38
Friday, December 16, 2011	190.97	182.27	194.27	212.12	200.72	208.02
Sunday, December 18, 2011	198.45	189.45	194.35	226.41	214.71	213.91

Wednesday, January 04, 2012	207.32	195.02	194.42	221.45	211.15	218.45
Sunday, January 08, 2012	204.06	196.96	201.46	220.06	208.46	216.96
Wednesday, January 11, 2012	195.83	182.83	196.73	212.72	200.42	202.42
Sunday, January 15, 2012	180.56	169.86	178.86	199.65	194.35	200.65
Wednesday, January 18, 2012	184.66	166.46	173.46	196.05	184.45	193.45
Sunday, January 22, 2012	174.76	159.96	162.86	188.94	174.84	183.04
Wednesday, January 25, 2012	123.96	112.76	118.16	141.10	136.30	137.20
Sunday, January 29, 2012	122.02	113.32	120.72	135.81	132.31	139.51
Wednesday, February 01, 2012	118.11	107.21	111.11	137.54	120.84	126.84
Sunday, February 05, 2012	111.18	101.28	106.18	136.40	122.80	129.50
Thursday, February 09, 2012	102.38	94.58	96.08	120.76	114.16	117.76
Sunday, February 12, 2012	107.04	88.24	92.84	113.66	106.76	110.96
Thursday, February 16, 2012	96.64	86.14	87.74	107.14	99.94	105.94
Sunday, February 19, 2012	92.01	80.01	90.31	105.22	102.32	103.92
Sunday, March 04, 2012	120.56	114.46	121.46	137.35	132.85	134.25
Thursday, March 08, 2012	130.67	119.77	132.47	148.69	134.79	142.69
Sunday, March 11, 2012	157.75	150.45	154.15	178.21	164.71	168.41
Thursday, March 15, 2012	208.92	196.72	194.92	252.33	239.23	246.93
Sunday, March 18, 2012	162.31	148.81	153.81	185.55	174.95	186.15
Tuesday, March 20, 2012	110.54	101.74	97.64	130.81	121.01	123.21
Sunday, March 25, 2012	205.73	186.93	192.63	230.27	223.47	222.87
Thursday, March 29, 2012	105.49	90.59	98.79	125.93	111.13	115.43
Sunday, April 01, 2012	90.52	87.12	82.92	117.79	106.69	119.69
Saturday, April 07, 2012	133.94	128.34	138.24	169.34	162.44	163.04
Sunday, April 08, 2012	202.43	185.93	198.93	239.94	229.64	227.94
Thursday, April 12, 2012	106.94	95.14	97.74	126.78	122.58	120.28
Wednesday, May 02, 2012	232.63	218.63	221.43	254.38	242.58	246.48
Friday, May 04, 2012	156.95	144.55	154.35	183.46	169.96	180.16
Sunday, May 06, 2012	141.16	128.26	131.16	161.31	151.31	159.31
Wednesday, May 09, 2012	150.25	143.75	148.45	167.79	154.99	155.69
Sunday, May 13, 2012	136.96	128.46	127.06	157.41	143.71	157.61
Wednesday, May 16, 2012	151.26	138.16	148.66	159.36	155.46	159.16
Sunday, May 20, 2012	170.00	153.10	164.50	182.05	173.35	178.25
Wednesday, May 23, 2012	195.46	183.36	194.96	209.72	197.82	207.12
Sunday, May 27, 2012	135.18	130.28	136.68	150.09	137.69	145.89
Wednesday, May 30, 2012	136.87	126.87	134.17	148.11	143.11	142.11
Sunday, June 03, 2012	119.74	106.34	114.64	128.10	122.80	127.60
Wednesday, June 06, 2012	111.64	94.24	105.54	116.11	110.81	111.61
Sunday, June 10, 2012	115.56	105.76	112.86	131.14	115.14	125.74
Friday, June 15, 2012	96.99	83.59	81.59	102.87	90.67	100.37
Sunday, June 17, 2012	108.35	94.15	100.45	116.28	106.68	115.58

Tuesday, June 19, 2012	110.82	97.42	108.22	113.77	107.67	115.27
Sunday, June 24, 2012	110.96	99.36	108.56	123.03	114.23	118.73
Wednesday, June 27, 2012	108.19	104.79	103.49	142.53	127.03	139.93
Sunday, July 01, 2012	112.13	101.13	111.13	126.48	114.38	119.38
Thursday, July 05, 2012	91.40	74.10	76.80	95.53	91.03	94.03
Saturday, July 07, 2012	96.72	86.12	96.62	103.57	94.97	100.37
Wednesday, July 11, 2012	116.04	98.04	112.14	126.86	116.36	121.46
Thursday, July 19, 2012	118.56	109.56	112.06	126.50	115.20	122.70
Saturday, July 21, 2012	124.66	109.46	115.26	137.24	126.24	128.34
Sunday, July 22, 2012	123.58	112.38	118.58	138.22	127.22	123.42
Wednesday, July 25, 2012	106.69	97.49	104.79	115.40	101.10	109.90
Tuesday, August 07, 2012	115.84	110.44	113.64	130.66	115.86	118.46
Saturday, August 11, 2012	117.06	100.26	114.26	124.71	112.81	122.71
Sunday, August 12, 2012	119.79	113.59	116.79	127.22	123.82	129.82
Thursday, August 16, 2012	86.88	72.88	78.38	94.17	83.47	86.77
Sunday, August 19, 2012	113.32	103.12	103.32	122.80	107.10	106.50
Tuesday, August 21, 2012	120.37	105.27	115.47	123.50	117.30	118.30
Sunday, August 26, 2012	136.37	123.97	130.47	146.11	133.61	140.01
Friday, August 31, 2012	100.35	86.25	96.95	110.59	100.69	95.09
Sunday, September 02, 2012	109.34	102.64	102.34	128.38	116.28	119.68
Wednesday, September 05, 2012	112.73	97.43	106.13	124.65	113.75	114.25
Sunday, September 09, 2012	88.95	76.45	87.35	98.13	83.73	89.33
Thursday, September 13, 2012	108.16	92.86	98.76	115.87	106.07	112.07
Sunday, September 16, 2012	104.47	97.17	104.47	118.04	102.74	115.04
Thursday, September 20, 2012	169.49	157.89	162.49	177.20	161.90	170.30
Thursday, October 11, 2012	106.74	97.94	102.24	116.74	111.84	112.74
Friday, October 12, 2012	111.28	98.78	113.28	130.59	116.99	113.99
Saturday, October 13, 2012	105.73	92.93	91.23	111.57	103.47	97.17
Sunday, October 14, 2012	102.54	94.84	103.14	118.60	108.50	114.50
Monday, October 15, 2012	114.45	108.55	109.25	131.16	121.46	128.06
Tuesday, October 16, 2012	104.72	90.52	102.72	118.60	105.00	113.10
Wednesday, October 17, 2012	95.42	85.52	97.22	107.33	94.53	100.93
Thursday, October 18, 2012	99.15	84.05	90.25	100.65	94.15	98.65
Friday, October 19, 2012	108.51	95.41	101.41	110.37	101.67	103.97
Saturday, October 20, 2012	108.44	100.54	97.04	116.41	109.41	107.21
Sunday, October 21, 2012	116.94	106.04	106.24	132.39	119.49	131.69
Monday, October 22, 2012	117.47	105.47	110.17	135.21	116.91	122.61
Tuesday, October 23, 2012	109.75	101.65	113.45	124.20	114.10	123.10
Wednesday, October 24, 2012	112.24	99.24	104.44	116.41	108.71	115.11
Thursday, October 25, 2012	103.31	96.51	100.51	118.17	107.47	108.67
Friday, October 26, 2012	108.81	91.91	100.21	110.65	104.25	101.45

Saturday, October 27, 2012	108.16	91.76	103.66	121.26	105.66	110.56
Sunday, October 28, 2012	105.20	91.30	100.40	112.25	99.55	104.85
Monday, October 29, 2012	109.51	94.31	108.31	118.96	109.16	110.76
Tuesday, October 30, 2012	102.73	88.63	98.63	115.52	99.12	110.72
Wednesday, October 31, 2012	118.56	102.46	120.36	132.65	119.65	125.35
Thursday, November 01, 2012	112.71	100.41	103.91	124.87	111.87	126.37
Friday, November 02, 2012	106.10	94.30	105.70	120.38	105.28	107.08
Saturday, November 03, 2012	115.34	101.64	110.24	126.41	119.91	120.91
Sunday, November 04, 2012	108.77	97.97	114.07	124.29	116.39	118.39
Monday, November 05, 2012	120.71	112.41	107.01	128.60	122.40	120.30
Tuesday, November 06, 2012	121.34	109.64	116.44	141.88	129.88	133.18
Wednesday, November 07, 2012	127.41	117.51	116.51	131.47	128.17	125.37
Thursday, November 08, 2012	126.27	110.97	120.97	136.69	123.09	125.99
Friday, November 09, 2012	123.53	108.03	111.33	127.14	118.34	125.64
Saturday, November 10, 2012	133.84	123.84	123.14	141.69	136.69	137.09
Sunday, November 11, 2012	133.12	121.02	127.62	142.27	135.77	143.57
Monday, November 12, 2012	128.24	119.44	123.84	136.53	124.13	131.43
Tuesday, November 13, 2012	172.14	163.84	160.14	192.46	174.86	183.76
Wednesday, November 14, 2012	136.42	126.52	131.42	155.10	147.00	143.30
Thursday, November 15, 2012	134.99	125.49	135.79	158.18	147.38	156.58
Friday, November 16, 2012	119.13	107.23	117.73	131.24	119.84	130.64
Saturday, November 17, 2012	128.06	111.76	123.86	139.21	127.01	138.01
Sunday, November 18, 2012	143.61	134.31	132.01	152.90	144.60	149.90
Monday, November 19, 2012	143.77	136.17	143.87	159.19	155.79	154.09
Tuesday, November 20, 2012	140.43	128.83	133.43	146.26	135.86	138.36
Wednesday, November 21, 2012	131.94	117.34	130.04	142.56	133.96	137.56
Thursday, November 22, 2012	161.88	151.48	147.18	165.58	155.08	164.58
Friday, November 23, 2012	177.29	166.19	161.79	188.71	170.71	174.41
Monday, December 03, 2012	139.49	131.39	139.49	155.68	149.98	153.08
Tuesday, December 04, 2012	140.37	127.87	134.87	156.87	146.37	151.47
Wednesday, December 05, 2012	160.78	147.18	150.88	171.19	162.39	167.79
Thursday, December 06, 2012	172.14	154.04	162.14	184.28	169.78	182.38
Friday, December 07, 2012	146.15	133.25	145.05	167.32	156.82	155.02
Saturday, December 08, 2012	155.77	142.77	152.77	168.98	153.28	162.18
Sunday, December 09, 2012	153.96	144.66	145.16	174.13	158.43	167.83
Monday, December 10, 2012	155.27	149.27	151.97	173.41	163.01	161.31
Tuesday, December 11, 2012	174.49	163.79	169.09	191.78	187.78	186.48
Tuesday, December 25, 2012	172.64	167.84	174.54	187.36	180.36	183.26

APPENDIX II

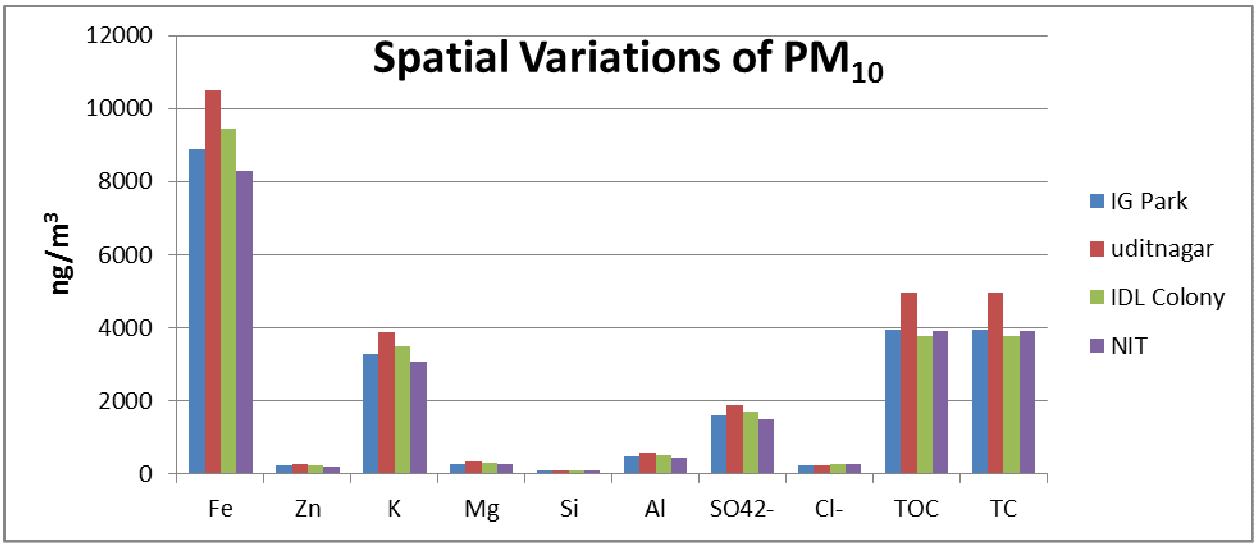
Source signatures used for source identification in Indian studies.

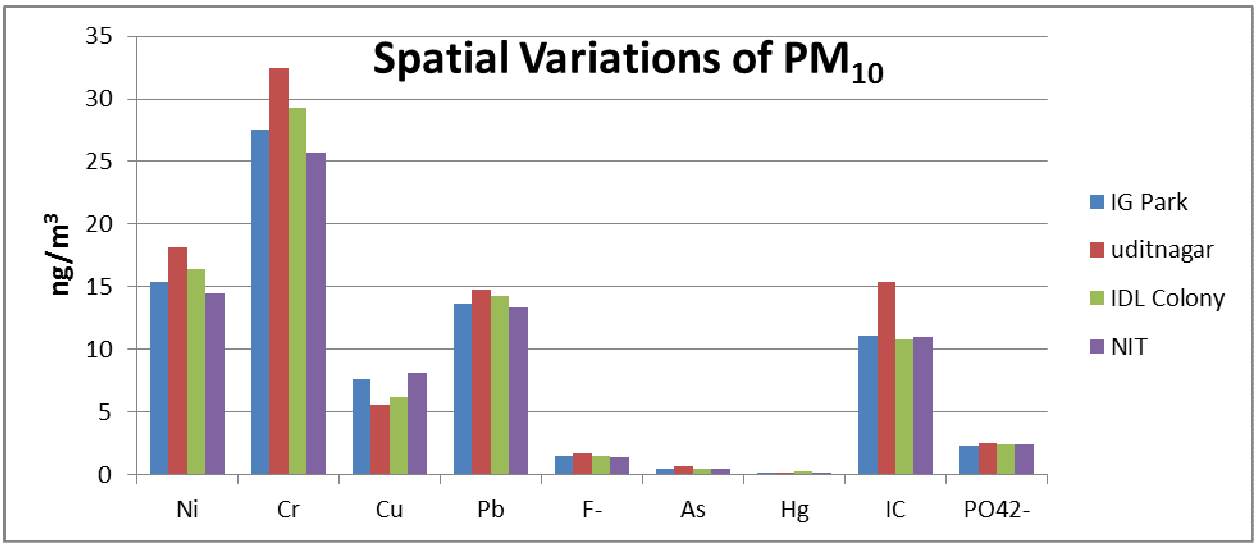
Source signature	Size fraction	Identified source	City	Reference
Na, Mg, K	SPM	Marine	Mumbai	(Kumar et al. 2001)
Na, K	PM_{10} divided into coarse and fine fractions		Mumbai	(Kothai et al. 2008)
Na, Cl	PM_{10}		Mumbai	(Chelani et al. 2008)
K	SPM	Biomass burning	Delhi	(Shridhar et al. 2010)
K, NH_4^+	$PM_{2.5}$		Jorhat	(Khare and Baruah 2010b)
As, SO_2	SPM	Coal combustion	Mumbai	(Kumar et al. 2001)
Co	TSP		Delhi	(Srivastava and Jain 2007)
Picene	$PM_{2.5}$		Delhi, Mumbai, Kolkata	(Chowdhury et al. 2007)
Te, S, Mn, Sn, Sb, SO_4^{2-}, Cd	PM		Jorhat	(Khare and Baruah 2010a)
Zn, Pb	TSP	Refuse/solid waste burning	Bombay (Mumbai), Bangalore, Nagpur, Jaipur	(Negi et al. 1987)
TC, OC, NO_3	PM_{10}		Kolkata	(Karar and Gupta 2007)
Cr, Ni	PM_{10} divided into coarse and fine fractions		Navi Mumbai	(Kothai et al. 2008)
Cu, Cr, Ni	$PM_{2.5}$ and PM_{10}		Agra	(Kulshrestha et al. 2009)
Zn, Pb	PM_{10}		Delhi	(Chelani et al. 2010)
Coarse mode of Pb, Cr and fine mode of Pb, Cr, Ni	PM_{10} divided into coarse and fine fractions	Vehicular/industrial	Delhi	(Balachandran et al. 2000)
Cd, Cr, Ni, Pb	SPM		Delhi	(Khillare et al. 2004)
Pb, Co, Sb	PM_{10} divided into coarse and fine fractions		Navi Mumbai	(Kothai et al. 2008)
Co, Ni, Cu, Zn, Cd, Te	$PM_{2.5}$		Jorhat	(Khare and Baruah 2010a)
Zn, Cu, Br,V, Mn	TSP	Industrial	Bombay (Mumbai), Bangalore, Nagpur, Jaipur	(Negi et al. 1987)
Coarse and fine modes of Ni, Cd	PM_{10} divided into coarse and fine fractions		Delhi	(Balachandran et al. 2000)
Cu, Mn, Ni	SPM		Mumbai	(Kumar et al. 2001)
Fe, Se, Mo, Sb with low loading of Cr, V, Mn, Cu	PM_{10}		Tirupati	(Chandra Mouli et al. 2006)
Mn, Cr	$PM_{2.5}$ and PM_{10}		Agra	(Kulshrestha et al. 2009)
Ni, Cd, Ba, Na	PM_{10}		Delhi	(Chelani et al. 2010)
Ni, Cr, Mn, Cu, Zn, Pb	TSP		Delhi	(Shridhar et al. 2010)
Co, Cr, Zn, Cu, Ni	TSP		Kolkata	(Kar et al. 2010)
Pb	TSP	Vehicular	Bombay (Mumbai), Bangalore, Nagpur, Jaipur	(Negi et al. 1987)
Pb, Cr, NO_2	SPM		Mumbai	(Kumar et al. 2001)
Cu, Pb, Cr	TSP		Delhi	(Srivastava and Jain 2007)
Cr, Pb, Ni, Mn, Fe	PM_{10}		Kolkata	(Karar and Gupta 2007)
Zn, S, BC	PM_{10} divided into coarse and fine fractions		Navi Mumbai	(Kothai et al. 2008)
Cu, Cr, Zn, Ni, Ca, Zn, Co	PM_{10} divided into coarse and fine fractions		Delhi	(Srivastava et al. 2009)
Cu, Zn, Pb	PM_1		Kanpur	(Chakraborty and Gupta 2010b)
Pb, Ni, Mn, Zn, Cu	$PM_{2.5}$ and PM_{10}		Agra	(Kulshrestha et al. 2009)
Cu, Ni, Co, Cr, Ca	TSP		Delhi	(Srivastava et al. 2009)
Zn	SPM		Mithapur	(Basha et al. 2010)
EC, OC, Zn	PM_{10}		Delhi	(Chelani et al. 2010)
Al, Si, Ca, Ti	TSP	Crustal dust/road dust/re-suspended dust	Bombay (Mumbai), Bangalore, Nagpur, Jaipur	(Negi et al. 1987)
Fine and coarse mode of Fe	PM_{10} divided into coarse and fine fractions		Delhi	(Balachandran et al. 2000)
Fe, Al, Ca	SPM		Mumbai	(Kumar et al. 2001)
High loading of Fe	SPM		Delhi	(Khillare et al. 2004)
Li, V, Cr, Mn, Ni, Co, Cu, Pb	PM_{10}		Tirupati	(Chandra Mouli et al. 2006)
Cl^-, SO_4^{2-}	PM		Kolkata	(Karar and Gupta 2007)
TC, OC, Fe	TSP (road dust)		Kolkata	(Gupta et al. 2007a)
OC, TC, Cl^-, SO_4^{2-}	TSP (soil dust)		Kolkata	(Gupta et al. 2007a)
Ni, Pb, Mn, Fe, Cu, Cd, Cr, Co	TSP		Delhi	(Srivastava and Jain 2007)
Fe, Cd, Zn, Ca, Cr, Ni, Mg, Ca	PM_{10} divided into coarse and fine fractions		Delhi	(Srivastava et al. 2008)
Fe, Sc, Si, Ti, Ca	PM_{10} divided into coarse and fine fractions		Navi Mumbai	(Kothai et al. 2008)
Mn, Mg, Fe, Al, V, Co	PM_{10}		Mumbai	(Chelani et al. 2008)
Cr, Zn, Cd, Mg, Ca	TSP		Delhi	(Srivastava et al. 2009)
Ca, Mg, Fe, Pb with moderate loadings of Zn, Cr, V	PM_1		Kanpur	(Chakraborty and Gupta 2010b)
Fe, Ni, Zn, Pb	$PM_{2.5}$ and PM_{10}		Agra	(Kulshrestha et al. 2009)

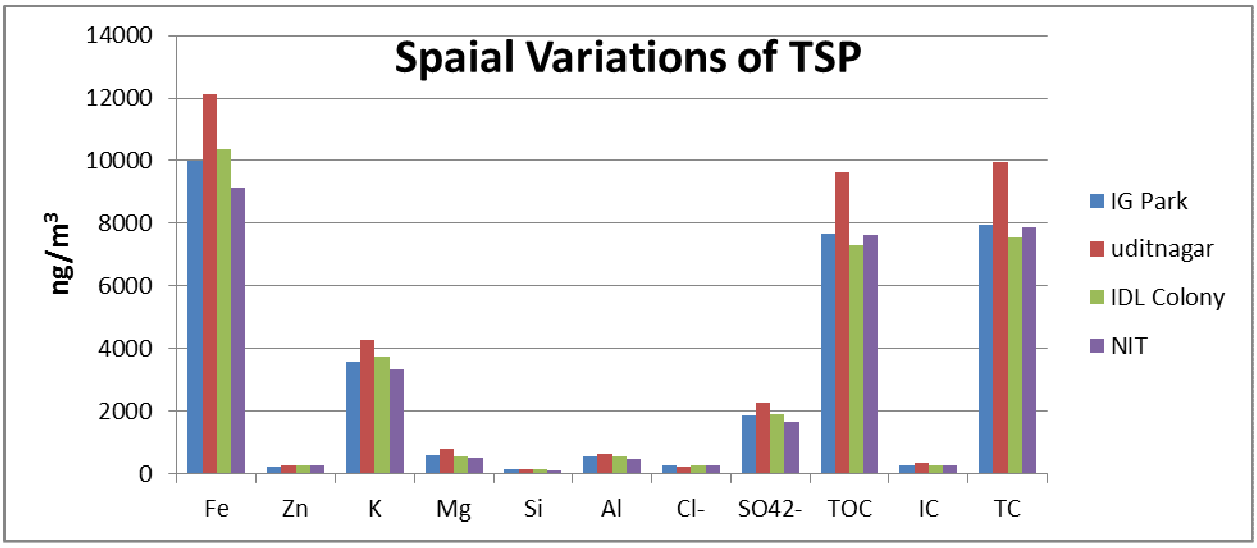
Al, Si, Ca, Ti	$PM_{2.5}$		Jorhat	(Khare and Baruah 2010a)
Ca, Mg, Fe, Al, Mn	SPM		Delhi	(Shridhar et al. 2010)
Pb, Cr, Co	SPM		Mithapur	(Basha et al. 2010)
Fe, Cr, Mn, K[b]	PM_{10}		Delhi	(Chelani et al. 2010)
Ca, Co	TSP	Construction activities	Delhi	(Srivastava and Jain 2007)
Fe, Pb, Ni	$PM_{2.5}$ and PM_{10}		Agra	(Kulshrestha et al. 2009)
Cd, V	SPM	Refuse oil burning	Delhi	(Shridhar et al. 2010)

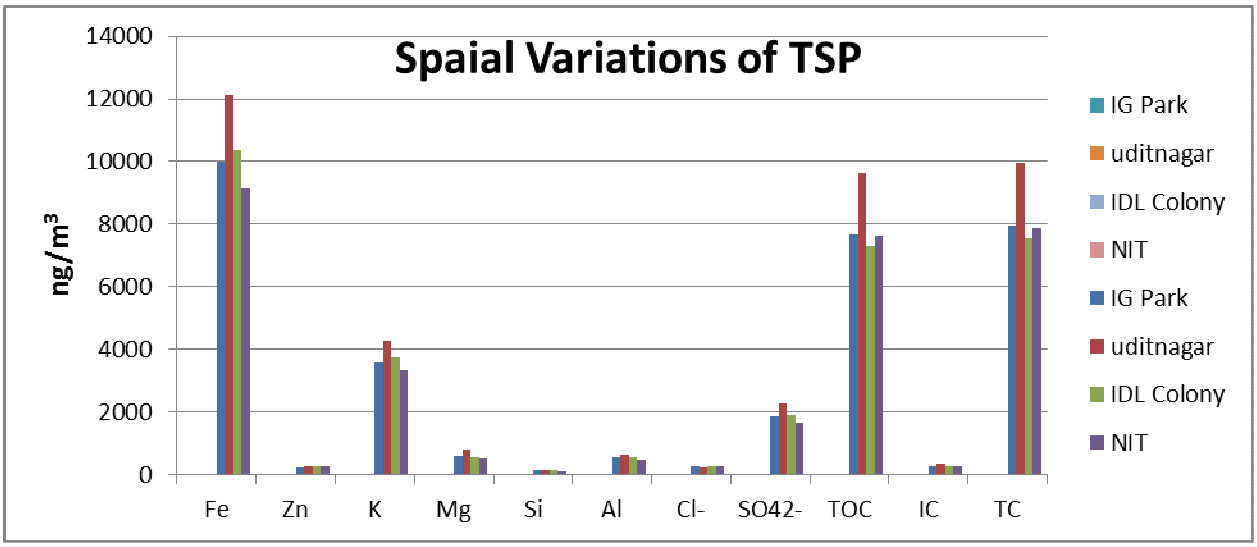
APPENDIX III

Spectial Variations of PM10 and TSP






Spaial Variations of TSP
ng/m³
14000
12000
10000
8000
6000
4000
2000
0
Fe
Zn
K
Mg
Si
Al
Cl-
SO42-
TOC
IC
TC
IG Park
uditnagar
IDL Colony
NIT


Spaial Variations of TSP
ng/m³
14000
12000
10000
8000
6000
4000
2000
0
Fe
Zn
K
Mg
Si
Al
Cl-
SO42-
TOC
IC
TC
IG Park
uditnagar
IDL Colony
NIT
IG Park
uditnagar
IDL Colony
NIT